THE

PHYSICAL SOCIETY

OF

LONDON.

PROCEEDINGS.

VOLUME XXVII.—PART I.

DECEMBER 15, 1914.

Price to Non-Fellows, **4s.** *net, post free* **4/3**.

Annual Subscription, **20/-** *post free, payable in advance.*

Published Bi-Monthly from December to August.

LONDON:
"THE ELECTRICIAN" PRINTING & PUBLISHING CO., LTD.,
1, 2 AND 3, SALISBURY COURT, FLEET STREET.

1914.

a platinum disc, P. B is a side tube, at the end of which is the arrangement described in my book on "Positive Rays," by which a photographic plate could be exposed to the radiation in the tube: a slit was placed in front of the plate, so as to get a definite image. The plates used were Schumann plates or plates specially prepared for me by the Paget Plate Company; these are not so sensitive to the radiation as the Schumann plates, and require a longer exposure; when, however, the radiation is strong enough they are more convenient to work with. L and M are two pairs of parallel plates 6·5 cm. long and 1 mm. apart, placed so that any radiation coming from A and striking the plate P must pass between L, while any radiation from P must pass through M before it reaches the photographic plates. These plates could be connected to a large battery of small storage cells, and a potential difference of 1,000 volts established between the plates in either pair.

When the positive rays were striking against the plate an exposure of a Schumann plate for an hour gave a dense photograph of the slit, showing that something was coming down the side tube which could affect a photographic plate. There are many well recognised types of radiation produced in A, and it is necessary to make further experiments to see if the photograph is produced by these or by some new type of radiation. It might be suggested, for example, that the effect had nothing to do with positive rays passing through the cathode to P, but was produced by ultra-violet light or Röntgen rays generated in the discharge-tube, which passed through the aperture in the cathode, and was then reflected from the platinum plate. If this were the case, since neither ultra-violet light nor Röntgen rays are deflected by an electric field, the intensity of the photograph should be the same whether the P.D. between the plates in L was zero or 1,000

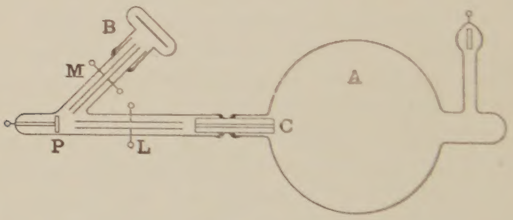


FIG. 1.

volts. It was found, however, that the photographic effect almost disappeared when there was a P.D. of 1,000 volts between the plates, showing that the effect is due to the positive rays. The effect, though reduced to a small fraction of its former value by putting on 1,000 volts, is yet not entirely eliminated. The small residual effect is due, I think, to the fact that the positive rays, except at the very lowest pressures, do not remain constantly positively charged, but alternate from the charged to the uncharged condition : thus a few of them might remain without charge all the time they were between the plates and thus escape deflection ; after passing through the plates they might re-acquire a positive charge before striking against P. I think this is more probable than that the residual effect is due to ordinary Röntgen rays or ultra-violet light produced in A, for the rays, as we shall see, are too easily absorbed by white fluorite to be ultra-violet light, and by thin mica or collodion to be ordinary Röntgen rays. Another proof that the effect is not due to stray radiation from A is that it disappears entirely if C is made anode instead of cathode.

One of the effects of the impact of positive rays against a metal plate is to make the plate emit slow cathode rays, and it might be thought that the effect on the photographic plate was due to these rays, starting from P and travelling down to the plate. If this were the case, then putting a P.D. of 1,000 volts between the plates in M ought to stop the effect entirely. I find, however, that the photographs are just as dark when 1,000 volts are on the plates as when they are at the same potential. This seems a conclusive proof that the radiation which affects the plate is not a corpuscular radiation or a form of positive rays, but is analogous to light or Röntgen radiations—that, in fact, Röntgen radiation is produced by the impact of positive rays against a solid.

This radiation is unable to penetrate even the thinnest films I have been able to procure of substances such as collodion, mica, paraffin-wax, aluminium, or white fluorite. When part of the slit was covered with one of these films it entirely stopped the radiation through that part of the slit. This radiation can be reflected, for if a slit of the kind shown in Fig. 2 is put in front of the photographic plate, it is found that the plate is affected not only underneath A, but also on the part to the left of the opening B. Part of this reflected radiation is corpuscular, as it is affected by a magnet ; a part of it is not so affected, and so must, like the incident rays, be a form of Röntgen radiation.

I should estimate the velocity of the positive rays at about 2×10^8 cm./second; the impact of cathode rays possessing the same energy as these would generate a very hard type of Röntgen ray; the type of Röntgen ray generated by the impact of positive rays more nearly resembles that produced by cathode rays with the same velocity, but much less energy than the positive rays.

I now pass on to consider the production of soft Röntgen radiation by the impact of slow cathode rays. The arrangement used is shown in Fig. 3. C is a Wehnelt cathode—a thin strip of platinum foil with a patch of barium oxide deposited on it by burning away a speck of sealing-wax. The anode A is a piece of brass rod with a hole bored through it, through which the cathode rays pass on their way to the target B, a copper plate which is at the end of, and in metallic communication with, a cylinder of wire gauze. The variation in the speed of the cathode rays was produced by putting between the gauze and the anode an E.M.F. tending to stop the rays. Thus, if V_1 is the P.D. between the anode and the cathode, V_2 that between the anode and the gauze, the energy of the cathode rays when they strike the target is proportional to $V_1 - V_2$. This method of varying the energy of the rays was found to work better than altering the potential between the cathode and the anode, as the emission of cathode rays from C was much more regular with a constant P.D. between the anode and cathode.

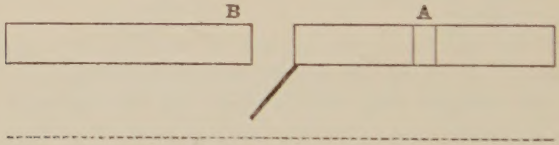


FIG. 2.

To detect the radiation coming from the target, a camera similar to that used in the previous experiment was placed at the end of the side tube T. A slit was placed in front of the plate, and half of it covered by thin slices of paraffin-wax, collodion, mica, glass, or fluorite so as to estimate the penetrating power of the radiation. A magnet was placed between the target and photographic plate so as to deflect from the latter any corpuscular radiation from the target. The vacuum was made as low as possible by means of charcoal and liquid air; it was so low that no luminosity could be detected between the anode and the target. The plates used were Schumann plates; the Paget plates were not sensitive enough to detect the radiation from the slowest cathode rays, though they gave good photographs when the rays fell through an effective potential of more than 100 volts.* The times of exposure, which varied from 1 minute to 2 hours, were chosen so as to make the energy in the cathode rays striking against the target during the time of exposure constant: thus with cathode rays which had fallen through 20 volts, the time of exposure would be 10 times that for those which had fallen through 200; the latter gave quite dense photographs with an exposure of 2 minutes.

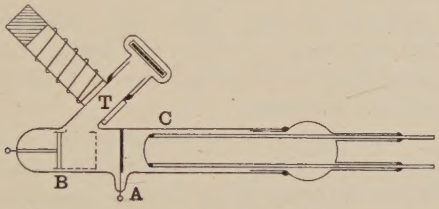


FIG. 3.

I have obtained photographs with cathode rays whose energy ranged from 10 to 600 volts, and there would be no difficulty in getting those corresponding to higher voltages by using larger batteries to produce the main discharge. These photographs are not due to ordinary light coming from the discharge-tube, for (i.) they are not obtained when the beam of cathode rays is deflected by a magnet from the target, and (ii.) the rays which produce them are unable to penetrate exceedingly thin films of glass To test whether they were due to a corpuscular radiation from the target two methods were employed. First, a magnet was placed between the target and the photographic plate, so as to deflect the corpuscular radiation from the plate; this did not affect the photographs. The second method was to place between the target and the photographic plate a pair of parallel plates similar to those used in the first experiment with positive rays, and apply to them a P.D. of 1,000 volts. The intensity of the photographs was not diminished when all the radiation which struck the plate had passed through this strong electric field, which would have stopped any charged particles.

---

* Since this Paper was read I have, by using a more copious supply of cathode rays, been able to get photographs at the lower voltages with Paget plates.

With regard to the penetrating power of this radiation, when it is produced by cathode rays with less energy than 40 volts, I have never been able to detect any photographic effect behind a film of collodion thin enough to show the colours of thin plates, paraffin-wax 4 μ thick, mica, or thin fluorite.* When the energy corresponds to 80 volts the effect behind the paraffin and collodion is appreciable, while with 200 volts and more there is very considerable penetration of the collodion and paraffin by the rays.

The great opacity of very thin films suggests that the frequency of the rays may be within the limits of those vibrations which, according to the usual theory of dispersion, are totally reflected by a medium.

According to this theory, if the medium has only one free period of frequency n, it is impervious to light, whose frequency p is given between the limits given by the equation,

$$p=n,$$

and

$$p^2=n^2+\frac{Ne^2}{m},$$

when N is the number of electrons per unit volume, e and m are respectively the charge and mass of an electron. This relation applies when the wave-length is large compared with the distance between the molecules ; and the limits ot opacity depend on the degree of closeness with which the molecules are packed : for example, in a gas they depend upon the pressure. In the case of Röntgen rays when the wave-lengths are small, or even comparable with the distance between the molecules, the case is different. The effect ot matter in this case is not so much to increase the refractive index as to scatter the radiation, and this scattering will be greatest when the atom is impervious to the radiation. If we apply the equation to the atom itself it indicates that the atom would be impervious to, and therefore scatter strongly, rays whose frequency is between limits which depend on the density of the electrons within the atom, and not on the closeness with which the atoms are packed.

---

* With larger currents from the Wehnelt I have been able to detect the photographic effect of the 40 volts rays behind thin collodion and mica, and also to detect the photoelectric effect and ionisation due to the rays which had passed through the films.

When there are more frequencies than one intrinsic to the atom, there will be several regions of great opacity separated by intervals of comparative transparency.

I am indebted to my assistants Mr. Everett and Mr. Eagle for the assistance they have given me in these experiments.

II. *On the Measurement of the Temperature Coefficient of Young's Modulus for Metallic Wires, with Special Application to Nickel.*

By E. Philip Harrison, *Ph.D., F.R.S.E., Indian Educational Service, Professor of Physics, Presidency College, Calcutta.*

Received May 28, 1914.

Introduction.

The problem of finding the variation of Young's modulus with temperature has always presented considerable difficulty, partly because small changes in temperature produce elongations in the material comparable with the stretches to be observed on loading and partly on account of the effects of the "after effect" (elastische nachwirkung) which becomes apparent at high temperatures.

To these special difficulties must be added the complexities common to the measurement of all elastic constants, such as anomalous changes in elasticity due to variations in the method of loading and annealing, or to the effect of the time during which a material has been subject to stress before its elasticity is measured. The fact remains that very little work has been published on the elastic constants of metals above 200°C., and none at all, so far as the present writer can discover, on nickel.

Of the earlier researches on the effect of temperature on elasticity the most important are those of Wertheim,* Pisati,† Katzenelsohn,‡ Macleod and Clarke.§

Pisati investigated Young's modulus for iron up to 300 deg., and expresses his results by means of a third degree empirical formula which shows a gradual diminution in the modulus as the temperature rises. Katzenelsohn experimented at lower temperatures, and Macleod and Clarke by heating a tuning fork and observing its changes in frequency deduce that the adiabatic modulus for steel decreases uniformly within the limits of their experiments. Wertheim also used an acoustical method.

---

* Wertheim, "Ann. Chim. Phys.," (3), Vol. XII., 1844.

† Pisati, "Gaz. Chim. Ital.," Vol. VII., p. 1; "Nuovo Cimento" (3), 4, 152, 1878; and 5, 34, 1879.

‡ Katzenelsohn, "Beiblatter," 12, p. 307, 1888.

§ Macleod and Clarke, "Phil. Trans. R.S.," Vol. CLXXI., Part 1, 1880.

Of more recent researches concerning the effect of temperature on Young's modulus only (apart from the important work of Horton and of Meissner on the rigidity modulus, or of Mallock on the bulk modulus) the following bear directly on the subject of this Paper :—

Miss Noyes * used a horizontally mounted wire, the distance between two scratches on which was determined by reading microscopes. The load was applied by adding weights to a scale pan connected to the wire by a string passing over a pulley on anti-friction rollers. Heating was effected, sometimes by a steam or hot-water jacket, sometimes by an electric current, and the experiments did not extend above 180°C.

It is claimed in the first Paper that Young's modulus varies with the temperature differently according to the method of electric heating employed. If the wire is heated by passing a current through it the modulus reaches a maximum at some temperature below 100 deg., but on heating by surrounding the wire with a helix conveying a current the modulus decreases uniformly with rise of temperature.

In the second Paper, using larger loads, the modulus was found to decrease uniformly whatever the method of electric heating. The author concludes that no detectable difference in the thermal coefficient is produced by magnetising the wire longitudinally or circularly.

Shakespear † used an interference method for measuring the stretch, and was thereby enabled to reduce the length of his specimen. The wires were heated by a steam jacket, and the temperature was measured by mercury thermometers.

He found that after a first heating the modulus was greater at higher than at lower temperatures, but that on repeated heating and cooling the material settled down to a steady state, in which Young's modulus decreased with rise of temperature. Gray Blyth and Dunlop‡ determined the variation of Young's modulus with temperature between 20 deg. and 100 deg. They used vertical wires 5 metres long, and heated with a steam jacket, reading the stretch with reading microscopes. Temperatures were measured by thermocouples. No maximum was found within the limits of their experiments, the results of which were similar to those of Shakespear.

---

* Noyes, "Physical Review," Vol. II., 1895, and Vol. III., 1896.

† Shakespear, "Phil. Mag.," Vol. XLVII., 1899.

‡ Gray Blyth and Dunlop, "Proc. R.S." Lond., Vol. LXVII., 1900, p. 180.

The modulus for steel at high temperatures was determined by Hopkinson and Rogers,[*] who heated a specimen $\frac{1}{5}$ in. in diameter and 4 in. long in an electric furnace. The experiments were carried up to 750 deg. in an atmosphere of nitrogen. Only six values of the modulus are given between 0 deg. and 750 deg., so that the authors are not in a position to express their results by means of a formula, but they find a decrease with rise of temperature and some evidence of a sudden increase in the temperature coefficient at 600 deg.

The difficulty of the experiments is increased by elastische nachwirkung, which is shown to increase with temperature. The authors claim definite values of the modulus even at 600°C. or 700°C., since they always used the " instantaneous extension " produced on first adding a load.

Wassmuth,[†] using a nickel wire, finds a value for the temperature coefficient up to about 100 deg. equal to $3 \cdot 26 \times 10^{-4}$.

A series of Papers by H. Walker[‡] describe experiments on Young's modulus between 0 deg. and 180 deg. A horizontal wire method is used, similar to that employed by Miss Noyes (*loc. cit.*), whose results are to a large extent confirmed and extended to other metals. The temperature of the wires was measured from their observed resistance, the resistance temperature coefficient being known from previous experiment.

The experimental portion of the wire used by Walker was about 1 metre long. It was enclosed in a glass tube, and the scratches on the wire were observed by microscopes through two holes bored in the glass.

The main results are as follows : When a metal is heated by the ordinary method (water jacket or vapour bath) Young's modulus decreases uniformly with rise of temperature ; when, however, the temperature is varied by passing a current through the wire, the resulting variation in the modulus depends on the load employed. When the latter is large the modulus changes as it does when heated ordinarily ; when the load is small both magnetic and non-magnetic metals show irreversible changes, which decrease to zero as the load is increased. Moreover, for small loads the modulus reaches a maximum below 100 deg. for electric heating only.

---

[*] Hopkinson and Rogers, " Proc. R.S." Lond., Series A, Vol. LXXVI., 1905.

[†] Wassmuth, " Akad. Wiss. Wien Sitz. Ber.," 115, 2a, pp. 223, March, 1906.

[‡] H. Walker, " Proc. R.S." Edin., 27, Part 4, No. 34, 1907 ; 28, Part 8, No. 40, 1908 ; 31, Part 1, No. 10, 1911.

Method employed in the Present Experiments.

The investigation described in this Paper was undertaken with the object of determining Young's modulus for nickel near its magnetic critical temperature, and was suggested by the fact that an anomaly in the temperature coefficient of expansion of that metal had been shown * to exist at about 370 deg. (a peculiarity subsequently investigated by Randall, and confirmed by Colby,† who used a Pulfrich interferometer). In my own experiments referred to above the wire under test had been stretched by a spring, the expansion coefficient at all temperatures being measured when the specimen was in a state of tension. It is a matter of some interest to discover to what extent, if at all, the expansion coefficient is modified by the existence of a load on the wire; one way in which this information can be obtained, apart from direct experiment, is by determining the temperature coefficient of Young's modulus and deducing therefrom the value of $d\alpha/d\mathrm{T}$, where α is the linear expansion coefficient of a metal under tension T. Thus a determination of Young's modulus at different temperatures up to 500°C. would supply the required information as to the relation between stress and the expansion coefficient, and, in addition, might be expected to decide whether or not any anomalous features exist in the neighbourhood of 370 deg.

To determine the stretch for a given load with the required accuracy in a length of wire sufficiently small to ensure reasonably uniform heating is a problem to which the optical method used by Shakespear is perhaps the best adapted; but the arrangements are elaborate, even at ordinary temperatures, while above 100 deg. the experimental difficulties are materially increased. It was, therefore, decided to use the reading microscope method, which had proved entirely satisfactory in finding expansion coefficients, and to modify the apparatus so that the necessary accuracy in the measurement of the stretch could be obtained on about 20 cm. of wire.

In view of the work of Miss Noyes (*loc. cit.*) it was thought legitimate to ignore the effects, if any, of circular magnetisation; consequently the specimen was heated directly by an electric current, its temperature being determined from its resistance. By using so short a length of wire the chance of

---

* Harrison, "Phil. Mag.," June, 1904.

† Colby, "Phys. Review," 30, pp. 506-521, April, 1910.

"patchy" heating due to inequalities in radiating power of the metal was much reduced, while pseudo stretches caused by want of perfect straightness in the wire are also negligible. With a length of wire so great as 1 metre, such as was used by both Miss Noyes and Walker, it appears almost impossible to eliminate the chance of such sources of error in measuring the modulus, especially at temperatures below 300 deg. or 400 deg.

As regards the position of the specimen to be tested, the alternative of suspending the wire vertically and hanging weights on to its end was discarded in favour of a horizontally stretched wire, for the following reasons :—

1. Uneven heating would be less likely to occur owing to the absence of air convection currents.

2. Errors due to "sag" are negligible in so short a length as 20 cm. ; in any case such errors could be calculated and allowed for (*see* Searle, "Experimental Elasticity," p. 88).

3. The difficulty of applying the stretching force and of estimating the effect of friction when the load is not applied directly to a freely hanging wire was overcome by means of a special apparatus designed for the purpose, in which a spring under compression was used to produce the stretching force. Moreover, various associated evils, familiar to anyone who has worked on the subject, were completely eliminated, such, for instance, as sudden jerks in the stretched wire, or the difficulty of keeping the wire continually in focus when taking a series of readings over a large range of temperature.

To sum up, the method used was to observe by means of reading microscopes the elongation of about 20 cm. of the central portion of a horizontally-stretched wire, heated electrically.

The temperature was measured by observing the resistance of the wire, and the stretching force was applied by a calibrated spring in conjunction with an apparatus specially designed to avoid friction and "wobbling."

It was decided that a pair of reading microscopes (1 in. objectives) with good micrometer eye-pieces were preferable to any form of microscope moving along a mechanical slide, since the former, in the first place, afford greater accuracy in reading, and, in the second place, the fact that the microscopes themselves are fixed during a series of measurements reduces the chance of accidental displacements to a minimum. In these circumstances, if the horizontal wire method is to give reliable results, the first necessity is for the specimen of wire to remain always in focus, notwithstanding changes in the stretching force or expansion by heat; for any readjustment of the focus is likely to alter the relative position of the microscope tubes, and thereby vitiate the results. To attain the required perfection in "focus" is was necessary to ensure that the wire when stretched or expanding should move truly parallel to itself.

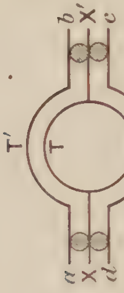
Many attempts were made to apply the stretching force by means of weights hanging over systems of pulleys (Noyes and Walker), or by means of spring balances of various patterns, but in every case the results were more or less unsatisfactory. Subsequently, as above remarked, the load was applied by a spring in compression, one end of which was fixed indirectly at one end of the experimental wire and the other to the other end. (*See* Fig. 1 (*a*), which is diagrammatic, and merely shows the principle of the arrangement.) The end *a* of the wire is fastened to a rod projecting centrally from and rigidly attached to the tube T. T slides inside another tube T′, to which the right-hand end *k* of the wire is fixed; thus, if a spring, C, in compression is inserted between flanges A and B on the left-hand ends of the two tubes, the wire is subject to a tension inversely proportional to the distance AB. A large number of measurements of Young's modulus at different temperatures were made with an apparatus of this type, in which the tube T slid without appreciable "shake" inside T′, the sliding surfaces being very accurately turned and polished; but difficulties due to friction, though not so great as might be imagined, were nevertheless considerable, and the apparatus was abandoned in favour of the modification described in the next section.

Detailed Description of the Apparatus.

The apparatus finally evolved is based on the above principle, but instead of the tube T sliding inside T′ *in the ordinary way*, a system of ball bearings was introduced in a manner which will be best understood, perhaps, with the help of the diagrammatic sketches shown in Fig. 1 (*a*) and (*b*).

The tube T is provided with two flanges, XX′, one at each side, which project freely through two horizontal slots (one of which is indicated by the dotted line in Fig. 1 (*a*) in the sides of T′).

a, *b*, *c*, *d* are plates rigidly attached to T′ and parallel to the flanges. In the top and bottom surfaces of the flanges are



Section of (a) at Y.

Fig. 1 (b).

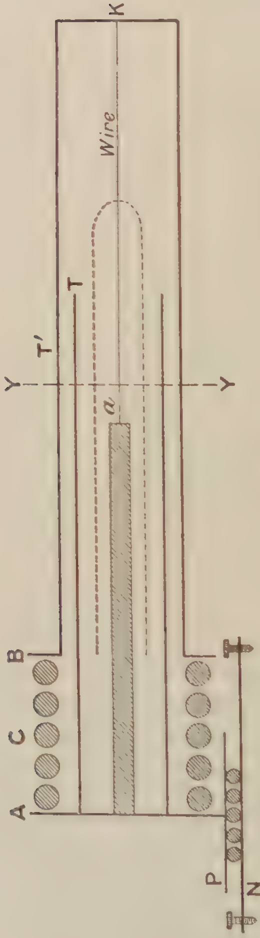


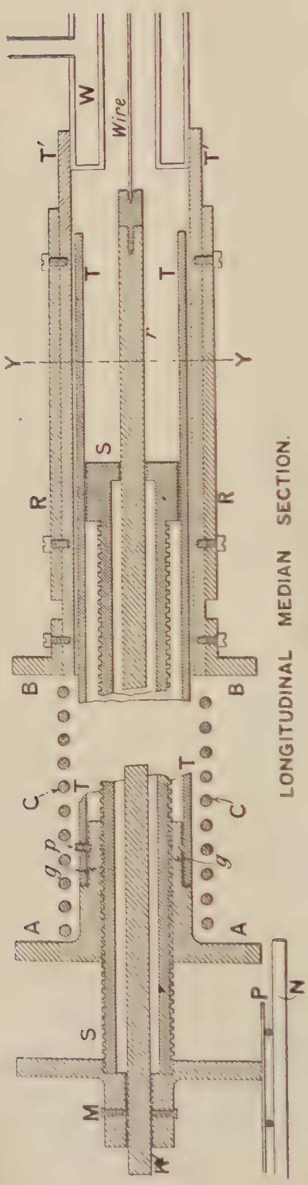
Fig. 1 (a).

machine-cut grooves parallel to the axis of the tube T, while corresponding parallel grooves run along the length of the approximating surfaces of the plates; thus between XX′ and the four plates four ball races are formed each occupied by a series of small steel bicycle balls.

The tube T is thus enabled to slide within T′, supported and guided by accurately parallel machine-cut ball bearings, with the result that the "focus" difficulty disappears, while at the same time all jerks and vibrations in the expanding wire are stopped and friction is reduced to a remarkable extent. The projecting end of T whose centre of gravity in the actual apparatus is well outside and to the left of T′ [Fig. 1 (*a*)] is supported by a plate, P, bearing by means of another parallel pair of ball bearings on a thick adjustable brass "table" N. This last detail was found to be essential to the success of the apparatus, since without it the bearings between T and T′ are apt to jam. When the instrument is in adjustment and the races well oiled the efficiency of the arrangement is very striking and, in the opinion of the writer, has rendered the horizontal wire method a most accurate and convenient one for the measurement of Young's modulus, or of an expansion coefficient.

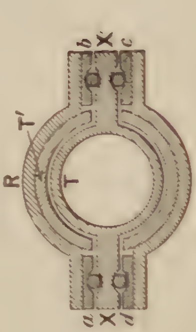
The above is a description of the principle on which the ball-bearing system was introduced. Many details have been omitted for the sake of clearness, but a drawing to scale of the complete arrangement is seen in Fig. 2 (*a*), the lettering of which applies also to the diagrammatic sketches in Fig. 1 (*a*) and (*b*). It will be seen that in practice the left-hand end of the wire is attached to a rod, *r*, which passes through a long hollow square threaded screw, *ss*. The rod *r* can be clamped at M or can slide freely without "shake" inside the screw. It is useful for purposes of adjustment. The steel compression spring C which applies the load to the wire bears on a screw nut A, working on *ss* while the nut A (and therefore the screw itself and the left-hand end of the wire) is attached to the sliding tube T. The nut is enabled, when it is screwed along *ss* to turn freely inside the tube T by means of the groove *g*, into which projects a screw, *p*; this arrangement allows A to rotate relatively to T but prevents relative motion along the axis of the tube. The reason for introducing the screw *ss* and the nut A is in order that the tension of the spring may be varied at will. It is clear that if A is screwed (say) from left to right—the right-hand end of the wire (not shown) being attached indirectly to T′—the spring is compressed and the load

Scale: Half full size.



LONGITUDINAL MEDIAN SECTION.

Fig. 2 (*a*).



CROSS SECTION AT Y.

Fig. 2 (*b*).

on the wire increased, while if A is moved in the opposite direction the load is reduced.

A water jacket, W (only a portion of which is shown in

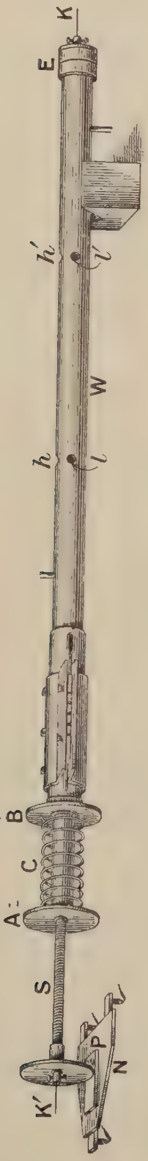


FIG. 3 (*a*).

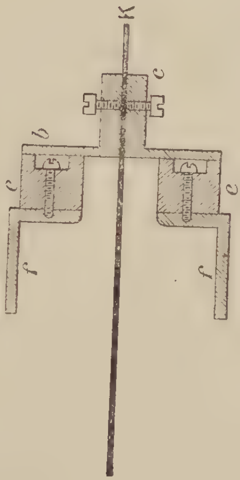


FIG. 3 (*b*).

Fig. 2 (*a*)), completely surrounds the wire and prevents the latter from heating up the reading microscopes and other apparatus. The right-hand end of the wire is fixed to the right-hand end of W. The simplest way to look at the somewhat complicated arrangement is to regard T, A, S and *r* as one system and B, T′ and W as another system capable of sliding freely relatively to one another, the two systems being tied together by the experimental wire and forced apart by the expansion of the spring C.

Fig. 3 (*a*) gives a general view of the whole apparatus, including the water jacket which surrounds the experimental wire.

The end piece E is shown in detail in Fig. 3 (*b*), and is necessary in order to insulate the two ends of the wire from one another, for the left-hand end is obviously in electric contact with the water jacket. E consists of a brass plate, *b*, carrying a clamp, *c*, separated by an ebonite block, *e*, from the brass cap *f* which screws on to the end of the water jacket. Thus, when the end piece is in position and the wire clamped at C, a heating current can be passed between K and K′.

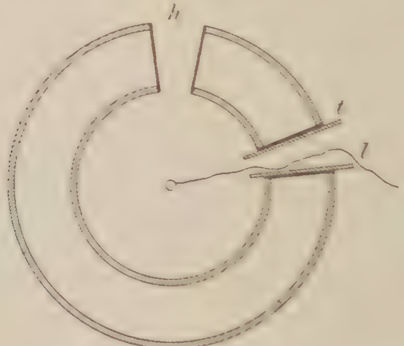


Fig. 4.

Four holes, *h* and *h*′, *l* and *l*′, pierce the water jacket. The former pair are for viewing the scratches on the wire; the latter are for illuminating purposes and for bringing out the potential leads used in the resistance measurement.

Fig. 4 is a cross section of the water jacket through *h* and *l* (or *h*′ and *l*′), showing the way the leads are brought out through glass tubes *t*, which do not interfere with the illumination.

The whole apparatus as shown in Fig. 3 (*a*) was mounted on the massive bed of a large comparator by Nalder Bros. with a pair of microscopes which could be firmly clamped in any position. In order to illuminate the reference marks on the experimental wire, two straight-filament electric lamps were supported near the illumination holes *l* and *l′*. Each lamp was completely surrounded by a cylindrical water jacket pierced with a hole through which the light could fall on the aperture *l* or *l′* in the apparatus. The water circulation was found necessary to avoid heating the microscopes and the observer.

The water jacket of the main apparatus as well as those of the two lamps were in series with a coiled tube surrounding a standard manganin resistance used in connection with the resistance measurements ; a continuous flow of water was kept up through the circuit during a series of observations.

Experimental Details.

General.—In making a measurement of the modulus at any temperature previous observers appear to have applied a definite load to the specimen and then to have read off the resulting elongation. The measurement was then repeated several times with the same load and the mean value of the stretches so observed was used to calculate the modulus.

The method used in the present research was to plot a load-elongation graph at each temperature, using a series of loads the greatest of which was well within the elastic limit* at that temperature. The probable error in the determination of the modulus obtained in this way is less than when a single load is applied, while additional information is supplied at each temperature as to whether Hooke's law is holding or not. The conclusion of Walker, for instance, that the elastic thermal coefficient is different for small loads from what it is for larger loads, is the same thing as stating that the load-elongation graphs are not linear over that range of temperature.

Measurement of the Stretching Force.

Calibration of the Spring.—By removing the cap E and attaching the wire, which thus passes freely out of the end of the water jacket to a specially constructed spring-balance arranged horizontally, the spring C was calibrated *in situ* under exactly the same conditions which prevail during an actual measurement of the modulus.

---

* *See* remarks on p. 27 as to the meaning to be attached to this expression.

The distance apart in centimetres of the flanges A and B (Fig. 1 (*a*)), was observed during the calibration.

The spring balance, in which friction was practically negligible,* had been previously calibrated in a vertical position, using 100 gramme steps.

The final calibration graph for spring C in which the distance between A and B was plotted against the tension of the spring in grammes weight proved to be a perfectly straight line within the limits of accuracy sought; this forms a good indication of the uniform nature of the extremely small frictional resistance of the ball-bearing slides.

Temperature Coefficient of the Spring.—An approximate measurement of this was made between 28° C. and 45° C. The maximum change in the temperature of the spring during one of the main experiments on Young's modulus was less than 5 deg., and it was found that the correction to be applied to the stretching force on account of changes in the elasticity of the spring was negligible.

Estimated Accuracy.—The distance AB was measured with a steel millimetre scale to $\frac{1}{10}$ mm., and, owing to slight mechanical irregularities in the flanges, was probably not correct to within $\frac{1}{5}$ mm. This means that the estimated error on a single observation of the force as read off from the calibration graph is equal to 20 grammes weight.

Measurement of the Elongation.

Considering the excellent definition of the microscopes and the fact that the wire when once mounted and annealed never got out of focus, it was found better to use small natural marks on the wire as reference marks† than to make artificial scratches. This method was not subject to accidental errors due to mistakes in identifying the marks, since any such mistakes would be detected at once when the load elongation graphs were plotted.

In all measurements the positions of the reference marks on the wire were read in terms of the "teeth" and fractions thereof in the micrometer eye-pieces; the readings were subsequently converted into centimeters by multiplying by the magnification factor.

---

* The spring of this balance was practically "free," the light index from its free end hardly touching the scale.

† *C.p.* Horton, "Phil. Trans." R.S., series A, Vol. cciv., p. 52.

The Magnification Factor.—This was found by placing a micrometer millimeter (by Zeiss) divided to fifths in the same plane as the surface of the wire and measuring the value of $\frac{1}{5}$ mm. in terms of "teeth" at several places along the scale.

The mean value found was 1 "tooth"=0·00423 cm.

The magnification was checked by similar measurements on the divided millimeter of a standard invar meter scale.

Estimated Accuracy.—The micrometers were read to 0·01 tooth, but since the setting of the cross-wire on a mark was probably doubtful to about twice this amount, the accuracy of *an individual reading* of a reference mark is estimated at not less than 0·02 tooth, or 0·00008 cm., which is about $\frac{1}{20}$th of the degree of accuracy obtained by Shakespear in measuring the elongation by an interference method.

Measurement of the Distance between the Reference Marks.

A standard invar meter was mounted so that its scale was in the same plane as the top surface of the wire. The actual distance apart of the central fixed threads of the eye-pieces was then determined at a known temperature. This distance was found to be 20·276 cm. at 28°C. A correction on the distance between the various pairs of reference marks used at different temperatures could then be easily applied since the actual readings of the reference marks on the toothed scale of each microscope was known.

It was seldom necessary to apply this correction, since marks were usually chosen which lay near the central thread.

Estimated Accuracy.—The length measurements were correct to 0·01 cm., which was much greater than was necessary in comparison with the other measurements.

Measurement of the Area of Cross-section of the Wire.

This was found at the end of the experiments by making a series of 76 determinations of the diameter at different places along the wire with a standard screw gauge. Another series of measurements was made on a portion of the fresh unheated wire. The difference of the means of these two experiments was 0·0002 cm. The probable error of the mean of each series was much less than this, so that it was legitimate to consider the determination of the cross-section as correct to 0·000004 sq. cm. throughout the range of the experiments.

The diameter from these measurements was 0·04298 cm., giving a mean cross-section of 0·001906 sq. cm.

Estimated Accuracy of the Determination of the Radius.—The radius was taken as being correct to 0·0001 cm. throughout the range, since the error on the radius due to expansion of the wire when heated through 400 deg. was of about the same value. The correct expression $\sqrt{\left(\frac{1}{r^2}\right)_{\text{mean}}} = \frac{1}{r}$ was not employed, as the difference between this and the ordinary mean did not affect the results to 2 per cent.

Adjustment and Determination of the Temperature.

General.—The most important, and perhaps the most difficult, feature of these measurements is to keep the temperature constant during the application of a series of loads.

That this is essential is easily recognised from the following calculation :—

If $l_2 - l_1$ is the change in length of the wire for a change of temperature of θ deg., we have $l_2 - l_1 = l_1 a\theta$ approximately, where a is the average coefficient of expansion over the range θ deg. $l_1 a\theta$ is the change in length due to temperature only; consequently, in order that changes in temperature may not vitiate the measurements of elongation due to loading, we must choose θ so as to make $l_1 a\theta$ small compared with the average increment of elongation produced by a load.

Taking the elongation increment as 0·001 cm. (which is less than the average) we must make $l_1 a\theta$ less than (say) $\frac{1}{10}$th of this. That is, θ must not be greater than 0·0001 $l_1 a$.

If we take a at 250 deg. as 0·000017,[*] and $l_1 = 20$ cm., we get the result that θ ought not to be greater than 0·3° C. This degree of steadiness was actually attained in the large majority of the measurements. When changes in temperature materially larger than this took place the measurements were discarded.[†]

A battery of large capacity storage cells was used to supply the current, and the series of constantan rheostats in the heating circuit, as well as the standard manganin comparison resistance, were immersed in oil.

---

[*] Harrison, "Phil. Mag.," June, 1904.

[†] *See*, however, p. 34.

As has already been stated, the experimental nickel wire was completely enclosed in a water-jacket through which a circulation was kept continuously running. The wire was thus effectively protected from draughts, and prevented from heating the apparatus in its neighbourhood.

Measurement of the Resistance.

Potential leads qq' of very fine platinum were silver soldered to the wire, each about 2 cm. beyond the reference marks mm' (*see* Fig. 5). The smallest possible quantity of solder was used so as to avoid disturbing the uniformity of the heating. These two leads were brought out of the water-jacket through the illumination holes. The resistance of the portion qq' of the nickel was determined by a potentiometer method, using as comparison standard a coil of No. 12 B.W.G. managnin immersed in oil and surrounded by a water circulation coil. The potentiometer was specially constructed for these measurements, and the various resistances were adjusted so that 1 mm. shift in the balance point corresponded to about 1°C. change of temperature in the nickel. Thus, in order to keep to the standard of temperature steadiness aimed at (0·3 deg.), observations were discarded (at least for the purpose of calculating the modulus) in which the balance point on the bridge wire changed by more than about 0·5 mm. It must be remembered, however, that such a degree of accuracy in the *measurement* of the temperature is by no means claimed. It was merely necessary for the temperature to remain constant to this extent during the observations.

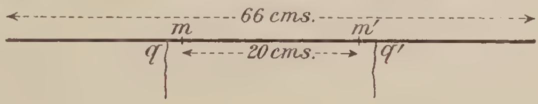


FIG. 5.

A sketch of the electrical arrangements is given in Fig. 6.

Measurement of the Temperature Coefficient of Resistance of the Nickel.

The specimen of nickel wire used in these experiments was good, but was not known to be of exceptional purity. It was, therefore unjustifiable to use the results for pure nickel already obtained by the writer in 1902.* Consequently a complete resistance temperature graph was constructed for the actual specimen employed in the Young's modulus experiments.

A suitable length of the nickel wire was wound into a spiral, fitted into a porcelain tube, and placed in an electric furnace side by side with a platinum thermometer. The two tubes were bound together with copper sheet, and their ends symmetrically placed in the centre of the furnace.

Temperature measurements were made by using the platinum thermometer in conjunction with a Callendar's recorder, corrections to air thermometer temperatures being applied graphically.

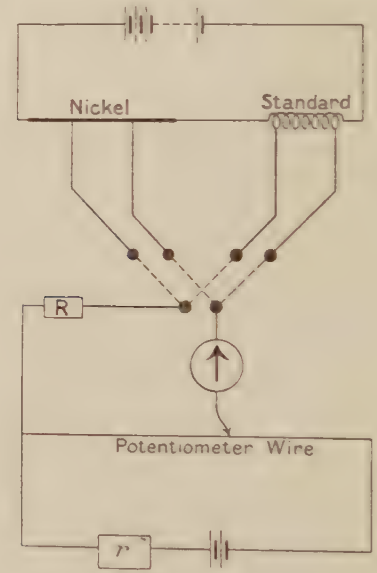


FIG. 6.

The resistance of the nickel at various temperatures was measured on the same potentiometer which was used in the elasticity experiments. The comparison coil was a 1-ohm standard immersed in a water bath.

The curve resulting from these resistance temperature measurements possesses a critical interval extending from

---

* Harrison, "Phil. Mag." S.R., Vol. III., No. 14, February, 1902.

365 deg. to 370 deg., a position which differs little from that found by the author for pure nickel (*loc. cit.* p. 24).

Estimated Accuracy.—The temperature measurements are correct to about 4°C. below 250 deg. and above 400 deg. Between 250 deg. and 400 deg. they are correct to about 3 deg. This follows from the fact that the resistance variation is more rapid near the critical temperature.

In view of the above degree of accuracy errors due to change of resistance of the wire by stretching or to changes of temperature of the standard manganin coil do not come in.

Discussion of the Accuracy of the Method.

Taking the value of Young's modulus (E) to be given by

$$E=\frac{fL}{\pi r^2 l},$$

where f is the stretching force in dynes, which produces an extension of l cm. in a wire of length L cm. and radius r cm., we have the following expressions for the proportional error ($\delta E/E$), produced in E by errors $\delta(f/l)$, δL, δr, in the quantities f/l, L and r respectively :—

Due to error in f/l—

$$\frac{(\delta E)_1}{E}=\frac{\delta f/l}{f/l}=\frac{l}{f}\delta(f/l) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Due to error in L—

$$\frac{(\delta E)_2}{E}=\frac{\delta L}{L}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Due to error in r —

$$\frac{(\delta E)_3}{r}=-2\frac{\delta r}{r}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now, suppose that a single observation of the stretch corresponding to a particular load is taken. It can be shown that the error on the quotient f/l, when f and l are subject to errors δf and δl respectively, is given by

$$\delta\left(\frac{f}{l}\right)=\pm\frac{\sqrt{\left(f\frac{\delta l}{l}\right)^2+(\delta f)^2}}{l},$$

where $\delta(f/l)$ is the error on a single observation of f/l.

Now, from p. 21 the value of δl for a single measurement is 0·00008 cm. and from p. 20 the value of δf for a single measure is 20 grammes weight; hence, taking $f=520$ grammes weight and the corresponding stretch $l=0{\cdot}0025$ cm. (as is the case for normal temperatures), we get

$$\delta(f/l)=\pm 10{,}000 \text{ approximately.}$$

Let it be assumed for the purposes of calculation that only five observations were made in obtaining a load elongation graph, then if each value of f/l is given the same "weight," the probable error of the mean of the five observations is

$$\frac{1}{\sqrt{5}}\,\delta\left(\frac{f}{l}\right)=4{,}600.$$

From expression (1) above, the percentage error produced in E by an error of 4,600 in measuring f/l is therefore given by

$$\frac{100\,(\delta E)_1}{E}=\frac{100\times 0{\cdot}0025\times 4{,}600}{520}=2 \text{ per cent.}$$

Again, from p. 21, the estimated error in L is 0·01 cm., so that from expression (2)

$$\frac{100(\delta E)_2}{E}=\frac{0{\cdot}01}{20}=0{\cdot}05 \text{ per cent.},$$

and from p. 22 the estimated error in r is 0·0001 cm. Hence, from expression (3),

$$\frac{100(\delta E)_3}{E}=\frac{2\times 0{\cdot}0001}{0{\cdot}0246}=0{\cdot}8 \text{ per cent.}$$

Combining these three it appears that the error on an individual measurement of Young's modulus, apart from the influence of errors due to temperature changes, is about 2 per cent., which is all that is required considering the temperature difficulties.

The above gives an idea of the accuracy of the method at ordinary temperature when the latter does not change by more than 0·3° C. At higher temperatures the probable error in the present research is slightly less than 2 per cent., owing to the existence of larger elongations for a given load.

If the length of the experimental portion of the wire were increased, and a somewhat larger spring employed, measurements of the modulus could easily be made to $\frac{1}{10}$th of 1 per cent.

Method of taking the Measurements.

The wire was annealed by heating electrically to about 500°C. under a tension sufficient to straighten out large kinks and bends in the wire. The temperature was then reduced to 300 deg., the load gradually and carefully increased at this temperature, the corresponding stretches being measured, and the process continued until no further anomalous elongations were observed (due to kink-straightening).

A load elongation graph was then determined at the temperature of the laboratory (about 27°C.).

The temperature was next raised to about 50 deg. and another graph obtained; and so on by steps of 30 deg. or 50 deg. up to 450 deg.

During the process a return was often made to lower temperatures. Throughout the range from 350 deg. to 430 deg., where anomalous features in the modulus were detected, the temperature intervals were much more frequent, and the measurements were made with continuously rising and continuously falling temperatures. As a rule, only one or two graphs could be obtained in one working day, as it took some time for the temperature to become steady, but throughout the course of the research the final form of the apparatus gave no trouble whatever, and when once in adjustment remains so indefinitely; as was emphasised before, the chief difficulties are connected with the temperature steadiness.

The total load on the wire varied from 2,000 grammes weight to 40,000 grammes weight up to a temperature of 200 deg., from 1,800 to 3,000 up to 350 deg. and from 1,600 to 2,800 up to 450 deg. The usual load increment applied was about 200 or 250 g.w. In forming a graph of load elongation, the actual load increment was plotted against the corresponding stretch in the experimental portion of the wire; up to 350 deg. a complete series of measurements included observations during unloading as well as during loading. Above this temperature the effects of elastische nachwirkung began to make themselves felt for the higher loads so that the graph for unloading was meaningless from the point of view of these experiments. In fact, all those portions of the graphs where the "after effect" became apparent correspond to what Hopkinson and Rogers call the "instantaneous extension," and this is what was employed in calculating the modulus.

When the graphs* had all been plotted, a load increment of 520 g.w. was chosen (equal to 1 cm. compression of the spring), and the corresponding stretches were read off from the graphs. The quotient of the corrected length† of the wire by the stretch gives L/l for each temperature; this is a quantity proportional to Young's modulus, and is shown in column 2, Table I.

The following table gives the data from which Fig. 7 was plotted :—

TABLE I.

Temperature of wire in degrees C.	$\frac{L}{l}$ (proportional to E).	$\frac{L}{l}\times 2·73$ E in kilos per sq. mm.
27·0	8,300	22,700
27·5	8,055	22,000
96·0	7,800	21,300
121·0	7,800	21,300
145·0	7,600	20,700
185·0	7,440	20,300
222·0	7,440	20,300
236·0	7,550	20,600
255·0	7,110	19,400
285·0	7,110	19,400
329·0	6,530	17,800
350·0	6,200	16,900
360·0	5,970	16,300
376·0	5,890	16,100
382·0	5,754	15,700
396·0	5,754	15,700
397·0	5,690	15,500
401·0	5,754	15,700
406·0	5,890	16,100
409·0	5,820	15,900
422·0	5,820	15,900
425·0	5,820	15,900
430·0	5,690	15,500
432·0	5,620	15,300
437·0	5,370	14,700
448·0	4,690	12,800
454·0	4,480	12,200
465·0	4,360	11,900

Length of the wire between the marks ...	20·276 cm.
Mean radius of wire..............................	0·04928 cm.
Mean cross-section..............................	0·001906 sq. cm.
Load increment	520 grammes weight.
Total minimum load	From 1,600 to 2,000 grammes weight.
Value of Young's modulus at 0° C. (by extrapolation)................................	22,200 kilogrammes/sq. mm.

---

* Typical examples are shown in Fig. 8, *a*, *b*, *c*, *d* and *e*.

† *See* p. 21.

The multiplying factor for converting L/l into E is, of course, $\frac{f}{\pi r^2}$, and is equal to $\frac{0{\cdot}520}{0{\cdot}1907}=2{\cdot}727$ kilos. per square millimetre. The values of Young's modulus so obtained are shown in column 3, and are expressed in kilogrammes per square millimetre. They are exhibited graphically in Fig. 7.

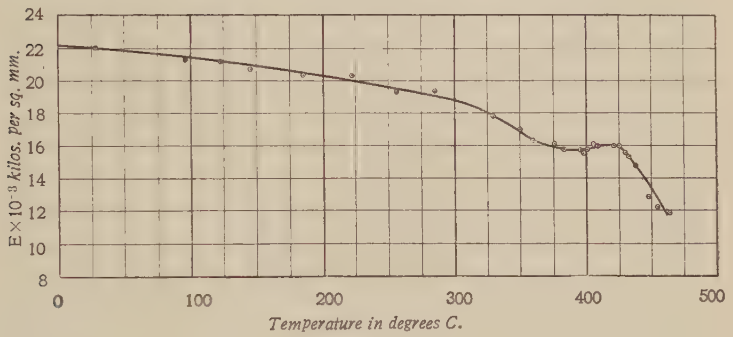


FIG. 7.

Discussion of Results.

General.—Up to about 300°C. the modulus for nickel diminishes slowly as the temperature rises. The results up to this temperature are represented well by the parabola

$$E_\theta=E_0(1-0{\cdot}000286\theta-0{\cdot}0000008465\theta^2),$$

where E=22,200 kilos. per square millimetre for the specimen used. This formula was calculated for the complete series up to 325 deg. by the Method of Least Squares.

Above 325 deg. the modulus begins to decrease rather more rapidly, reaching a minimum just below 400 deg. It then appears to increase again slightly, or at least to remain nearly constant up to 425 deg., after which a rapid diminution occurs.*

Too much stress ought not to be laid on the existence of an actual *minimum* at 390 deg., but the large number of observations above 350 deg. taken on different days with temperatures both rising and falling seems to establish with certainty the existence of a stationary value between 375 deg. and 425 deg. with less certain evidence of an actual minimum value. It is

---

* 400 deg. and 325 deg. are the mid-points of the temperature ranges throughout which T. A. Lindsay ("Proc." R. S. Edin., 29, 1908–1909) found important evolutions of heat to occur in Ni on cooling.

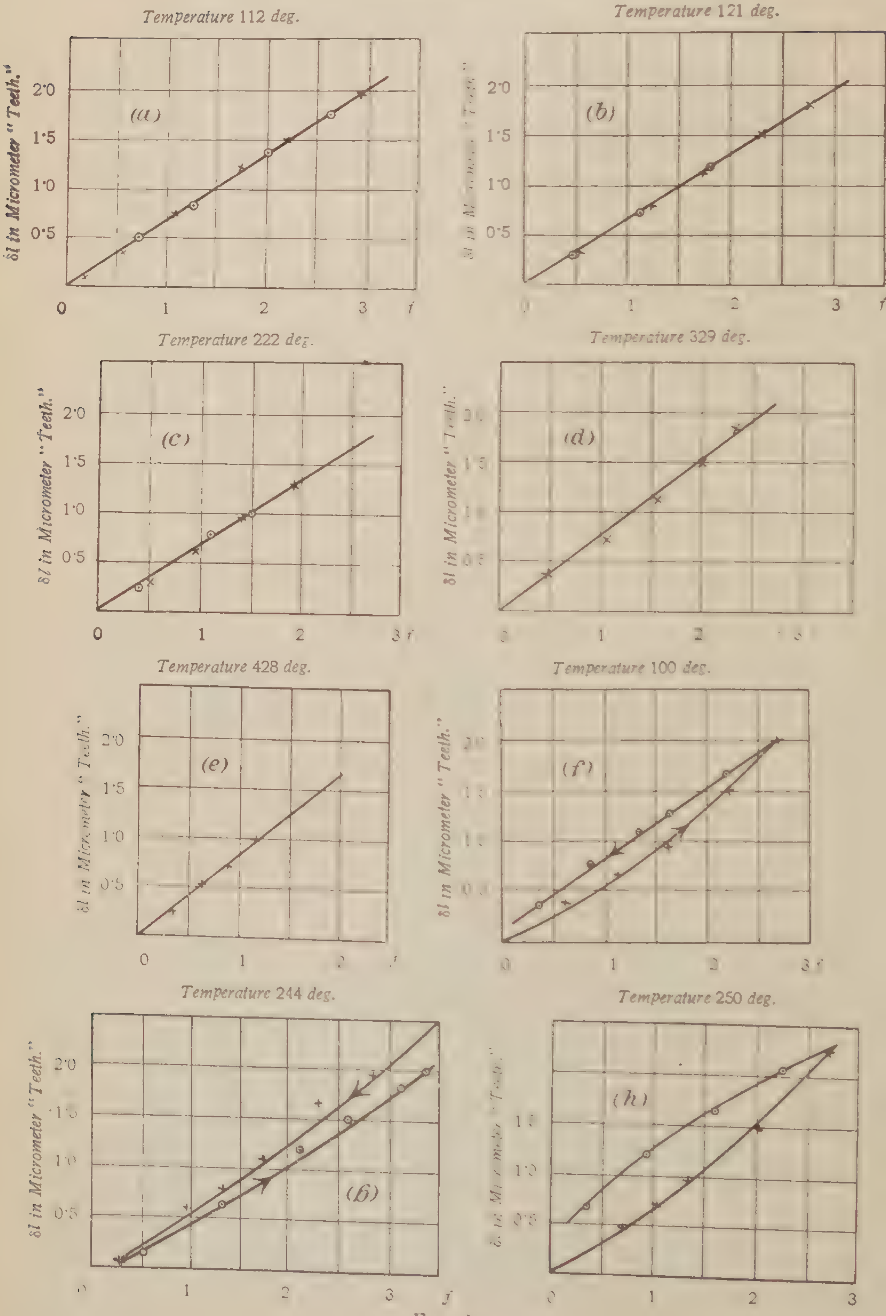
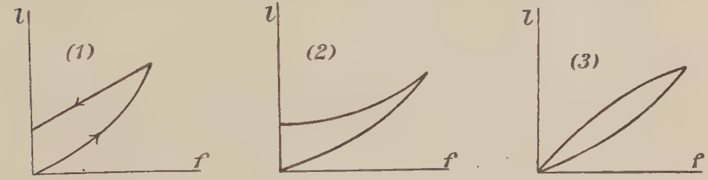

Temperature 112 deg.
(a)
δl in Micrometer "Teeth."
2·0
1·5
1·0
0·5
0
1
2
3
f
Temperature 121 deg.
(b)
2·0
1·5
1·0
0·5
0
1
2
3
f
Temperature 222 deg.
(c)
δl in Micrometer "Teeth."
2·0
1·5
1·0
0·5
0
1
2
3
f
Temperature 329 deg.
(d)
δl in Micrometer "Teeth."
1
2
Temperature 428 deg.
(e)
δl in Micrometer "Teeth."
2·0
1·5
1·0
0·5
0
1
Temperature 100 deg.
(f)
δl in Micrometer "Teeth."
0
1
2
3
f
Temperature 244 deg.
(g)
δl in Micrometer "Teeth."
2·0
1·5
1·0
0·5
1
2
3
f
Temperature 250 deg.
(h)
1
2
3

Fig. 8.

clear that the beginning of this constant value of the modulus coincides with the beginning of the critical interval in the resistance of the metal.

The Load Elongation Graphs (Fig. 8, *a*, *b*, *c*, *d*, *e*, *f*, *g* and *h*).—In general these were linear at all temperatures (*see* the examples shown in Fig. 8, *a*, *b*, *c*, *d* and *e*), but in certain experiments (*see* Fig. 8, *f*, *g* and *h*) the relation between load and extension was not found to be linear; moreover, the curve for unloading did not coincide with that for loading.

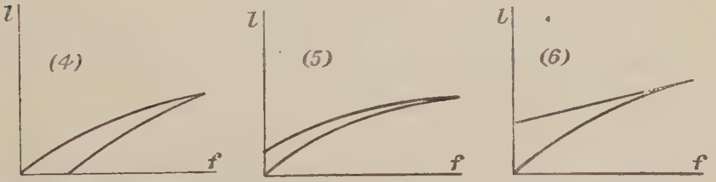
In cases in which non-linear graphs were obtained, different types appeared on different occasions, but these invariably conformed to one or another of the six types shown in Fig. 9, which represent diagrammatically the obvious effect of a gradually changing temperature on an otherwise linear load elongation graph. It will be noticed that *f*, *g* and *h* are of the type shown in Fig. 9, Nos. (1), (5) and (3) respectively.



Temperature rising during loading; constant during unloading.

Temperature rising during loading and unloading.

Temperature rising during loading; falling to its original value during unloading,



Temperature falling during loading and unloading.

Temperature falling during loading and rising during unloading.

Temperature falling during loading; rising during unloading.

FIG. 9.

It is true that curves similar to Nos. (1) or (3) might be produced by the "after-effect" alone, provided the latter set in at some stage during loading, but in the instances referred to, not only was there no appreciable "after-effect," but the observations *when repeated under constant temperature conditions* *invariably gave a linear graph in which the values of the stretches during loading coincided with those during unloading.*

The most usual form of non-linear graph obtained was like Fig. 9, Nos. (1) and (3), and in every instance of the kind it was evident from changes in the electric resistance of the wire that a slight rise, followed by a slight fall or by constancy in temperature, had occurred during the experiment.

The author, although misled at first by the regularity of such curves as *h* (Fig. 8) into a belief that they represented a genuine phenomenon connected with the elasticity of the metal, has now reached the conclusion that all the looped load elongation curves obtained in this research are due, not to an irreversible elastic effect, but merely to temperature changes. And this notwithstanding the experiments of J. O. Thomson* (who shows that increase in length is not exactly proportional to the stretching force) seeing that the effects claimed by Thomson are very much smaller than those at present under discussion.

It is interesting that Shedd and Ingersol† obtained curves for indiarubber at different temperatures of a similar kind to those in Fig. 8, No. *f*, *g*, *h*, but insufficient evidence is quoted as to the constancy of the temperature, so that in the absence of further information the present writer is not quite satisfied that Shedd and Ingersol's results cannot be explained as the result of temperature variations.

When a wire is stretched the temperature effect produced is always such as to increase the elasticity and thereby to oppose the stretch. If it be conceded, as a result of the present experiments, that the temperature coefficient of elasticity continually decreases up to 400 deg., then up to this temperature a stretch produces a fall of temperature in the wire. Hence, during loading adiabatically the temperature would be expected to fall slightly and to increase again on unloading, giving rise to the appropriate contraction and expansion in the metal. This effect, although it was actually detected in a few instances, is in general far too small to afford any explanation of the want of linearity of the load elongation graphs.

It is therefore concluded that, within the limits of accuracy discussed on pp. 21, *et seq.*, the present experiments show that the elongation of a nickel wire increases in direct proportion to the load, provided the "instantaneous extension" is employed in all cases in which the "after-effect" is apparent. The above conclusion seems to be at variance with the results both of Miss Noyes and of Walker, who suggest that the thermal coefficient may be smaller for a small load than for a large one. Shakespear regarded effects of this nature as holding only during the first few heatings of a wire, the latter settling down to a steady state after repeated heatings and coolings, and although the present writer cannot confirm this the point is not to be regarded as settled, for if Thomson's results are accepted and hold for different temperatures some small effect of the kind claimed by Miss Noyes and by Walker may really exist. It is noteworthy that Walker quotes an incredibly small value for Young's modulus for nickel (about 14×10^{11} at 16°C.). On calculating the average thermal coefficient of the modulus from his results I find 0·06 dyne per square centimetre per degree C., which is 200 times the value given by any of the few observers who, to my knowledge, have worked on the subject

---

* Thomson, "Wied. Ann.," 44, 1891.

† Shedd and Ingersol, "Phys. Rev.," Vol. XIX., p. 107, 1904.

Secular Effects.

It seems likely that above 425 deg. some structural change, possibly crystalline, occurs in the metal, and that this change sets in at the beginning of the critical interval, for at 425 deg. the wire is approaching the condition in which Hooke's law ceases to be true and small loads produce a permanent stretch *which does not recover with time.*

Below 400 deg. or thereabouts, when the load exceeds a certain value the influence of "elastic after-effect" becomes increasingly apparent as the temperature rises (*c.p.* Hopkinson and Rogers), but if time for recovery is allowed the wire returns to its original length, but not to its original condition as regards elasticity. It is slightly hardened by the process. Horton noticed an analogous effect in dealing with the rigidity of metal wires (*loc. cit.*).

Consequently it appears that unless a load is sufficient at any particular temperature to induce appreciable "after-effect" no important effect is produced on Young's modulus by the resulting stress, whereas if the "after-effect" has once occurred, a higher temperature is needed to wipe out the resulting hardening.

These remarks apply to temperatures below 425 deg.; probably they do not hold above that.

If the load is so small that no "after-effect" is noticeable, it appears that the metal is softened by heating to 400 deg. or 500 deg., but that it recovers with time.

In a metal which has no critical temperature possibly the transition to the condition found in nickel above 425 deg. is gradual instead of abrupt.

Values of $\frac{da}{dT}$.

It follows* from the definitions of Young's modulus (E) and the coefficient of linear expansion (a) that

$$\frac{da}{dT} = \frac{d}{d\theta} \cdot \frac{1}{E} = -\frac{1}{E^2} \cdot \frac{dE}{d\theta}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where T is the tension on the expanding wire.

Hence, obtaining the value of $\frac{dE}{d\theta}$ from the formula

$$E_\theta = E_0(1 + A\theta + B\theta^2),$$

and substituting in equation (4), we get

$$\frac{da}{dT} = -\frac{E_0}{E^2}(A + 2B\theta),$$

whence, adopting the values of A and B from the formula on p. 29,

$$\frac{da}{dT} = \frac{E_0}{E_\theta^2}(0{\cdot}000286 + 0{\cdot}00000169\theta).$$

Calculating this for various values of the temperature, the following table is obtained, which, of course, applies only (strictly speaking) to the particular specimen of nickel used in this research :—

TABLE II.

θ.	E_θ in kilos. per square millimetre.	$\frac{da}{dT} \times 10^8$.
10	22,180	1·37 deg.$^{-1}$kilo^{-1}mm.^{2}
100	21,840	2·09 ,,
200	20,220	3·37 ,,
300	18,650	5·08 ,,

$E_0 = 22{,}200$ kilos./sq. mm.

---

* Searle, "Experimental Elasticity," p. 74, Chap. III.

The values of column 3 are shown plotted against the temperature in Fig. 10.

Expressing $\frac{da}{dT}$ as a parabolic function of θ,

we have
$$\frac{da}{dT}=a+b\theta+c\theta^2.$$

Integrating this on the assumption that $\frac{da}{dT}$ is independent of T,

$$[a_\theta]_T=(a+b\theta+c\theta^2)T+P,$$

where P is a constant and is a function of θ.

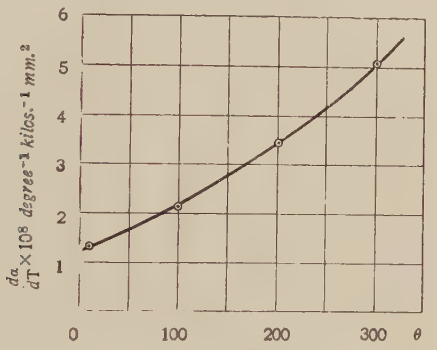


FIG. 10.

If $[a_\theta]_0$ is the value of a when T=0 we find $P=[a_\theta]_0$, so, finally

$$[a_\theta]_T-[a_\theta]_0=(a+b\theta+c\theta^2)T=T\left(\frac{da}{dT}\right)_\theta:$$

Where $\left(\frac{da}{dT}\right)_\theta$ is the value of $\frac{da}{dT}$ at temperature θ.

Since we know from Fig. 10 the variation of $\frac{da}{dT}$ with θ, it is simplest to keep the equation in the form

$$[a_\theta]_T-[a_\theta]_0=T\left(\frac{da}{dT}\right)_\theta. \quad \text{. . . . . .} \quad (5)$$

and to calculate $\frac{da}{dT}$ graphically.

To express this equation in terms of the actual expansion of the wire, let the temperature of the wire change from 0 deg. to θ deg. Then, when the tension is zero,

$$[a_\theta]_0=\frac{1}{l_0}\frac{\delta l_0}{\delta\theta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where l_0 is the length at 0 deg. and δl_0 is the expansion for change of temperature $\delta\theta$, both measured under zero tension.

When the tension is T kilos./sq. mm.

$$[a_\theta]_T=\frac{1}{l_T}\frac{\delta l_T}{\delta\theta},$$

when l_T is the length at 0 deg., and δl_T is the expansion for change of temperature $\delta\theta$, both measured under tension T.

Now, by definition of Young's modulus,

$$E=\frac{Tl_0}{l_T-l_0} \text{ at } 0°\text{C.},$$

or

$$l_0=l_T\left(\frac{E}{T+E}\right),$$

so the equation (6) becomes, on substituting for l_0,

$$[a_\theta]_0=\frac{T+E}{l_T E}\cdot\frac{\delta l_0}{\delta\theta},$$

whence, substituting this value and that for $[a_\theta]_T$ above, in equation (5), we have

$$\delta l_0=\frac{E}{T+E}\left[\delta l_T-l_T\,.\,\delta\theta\,.\,T\left(\frac{da}{dT}\right)_\theta\right];$$

or, since $\frac{E}{T+E}$ for tensions of the order employed is sensibly unity, we have finally

$$\delta l_T-\delta l_0=l_T\,.\,\delta\theta\,.\,T\,.\left(\frac{da}{dT}\right)_\theta. \quad . \quad . \quad . \quad . \quad (7)$$

Equation (7) gives the difference between the expansion under zero load and under a load T kilos. per square millimetre, when the temperature changes from 0 deg. to $\delta\theta$.

The result is not appreciably different if we regard the temperature change $\delta\theta$ to occur at any point along the temperature scale provided l_T is then taken as being the length under tension T at the lowest temperature of the range.

Suppose, as an example, it is required to find the expansion under zero load for a nickel wire of length about 10 cm. at 100°C, when the value of the expansion under a load of 8 kilos. per square millimetre is known by experiment. We then have

$\delta\theta = 100.$
$E = 22{\cdot}2 \times 10^3$ at 0° (by present experiments).
$T = 8$ kilos. per square millimetre.
$\delta l_T =$ increase in length for 100 deg. under load T.
$= 0{\cdot}014$ cm. by experiment.
$l_T = 10{\cdot}32$ cm. under tension T at 0 deg.
$\left(\frac{da}{dT}\right) = 1{\cdot}64 \times 10^{-8}$ taken from the curve Fig. 10 at 50 deg, the mean temperature of this range.

Then, from equation (7),

$$\delta l_T - \delta l_0 = 10{\cdot}32 \times 100 \times 8 \times 1{\cdot}6 \times 10^{-8} = 0{\cdot}00136 \text{ mm.}$$

Apparently the only direct experiments on the measurement of $\frac{da}{dT}$ are those of Bottomley. That observer found an extra extension of 0·14 mm. on about 500 cm. of copper wire due to a load difference of about 8 kilos. per square millimetre and a temperature difference of about 80°C.

This gives $\delta l_T - \delta l_0 = 0{\cdot}003$ mm. on 10 cm., showing that although no direct experimental data for $\frac{da}{dT}$ for nickel are as yet available, the effect obtained by Bottomley for copper is of the same order as that found theoretically for Ni from the present experiments on the temperature coefficient of Young's modulus.

Summary of Results.

1. A parabolic empirical formula is obtained which expresses the relation between Young's modulus and the temperature for nickel up to 300°C. An anomalous change is found to occur in the temperature coefficient of the modulus at the same temperature as the magnetic, thermo-electric, resistance and expansion critical points, namely, between 365 deg. and 425 deg.

2. Hopkinson and Rogers' result, that the "elastic after-

---

* Bottomley, "Phil. Mag.," Vol. XXVIII., 1889.

effect" in steel increases with temperature, is shown to be also true for nickel.

3. When the temperature is constant and the "elastic after-effect" is absent or allowed for, load elongation graphs are found to be linear, showing (*a*) that no appreciable irreversible effects are produced on loading and then unloading, (*b*) that the elastic temperature coefficient is the same for all loads employed during the research.

This is in conflict with the results of several other observers, as is also the fact that no maximum value in the thermal co-efficient just below 100 deg. was detected, even with the smallest loads employed, which were half the value of the smallest load used by Walker. It is true, however, that the question of the existence of a maximum was not very specially investigated during the course of the present research.

4. The value of $\frac{da}{dT}$, where a is the coefficient of expansion under tension T, is deduced from the thermal coefficient of Young's modulus obtained. It can be expressed as a parabolic function of the temperature.

Hence a formula is determined which gives the difference (at any temperature) between the expansion due to heat when the wire is free and when it is subject to a load T.

I am much indebted to Dr. W. A. K. Christie, of the Geological Survey of India, for giving me the specimen of nickel with which the above experiments were carried out.

Baker Physical Laboratory,
Presidency College.

III.—*A Bridge for the Measurement of Self-Induction in Terms of Capacity and Resistance.* By DAVID OWEN, *B.A. (Cantab.), B.Sc. (Lond.), Lecturer in Physics, Birkbeck College, London.*

RECEIVED OCTOBER 1, 1914.

1. The object of this Paper is to introduce an alternate-current bridge method of measuring inductance. This bridge is simple both in theory and practice, and proves to be adapted to accurate measurement over the whole range from a microhenry upwards.

The use of alternating current for the accurate measurement of inductance or capacity has many advantages. The revolving commutator allows of an increase of sensibility in bridge methods where direct current is applied, but introduces a somewhat delicate and complex piece of apparatus, the use of which is obviated by applying to the bridge an alternating voltage at the outset. Where the formula of calculation is independent of frequency the method has the advantage of being unencumbered by the determination of that quantity; and, furthermore, very good work is rendered possible with no source of current more elaborate than a buzzer or small induction coil. Sensitive means of determining the attainment of a balance are available in the telephone, the vibration galvanometer and the alternating-field moving-coil galvanometer

2. *The Proposed Bridge.*—The bridge (represented in Fig. 1) serves for the determination of self-induction in terms of capacity and resistance; or, alternatively, for the measurement of capacity in terms of resistance and a standard of self-induction. We will proceed by regarding the determination as that of a self-induction L. This is placed in the second arm BC of the bridge in series with an adjustable non-inductive resistance, making up the total resistance of the arm to r_2. In the first arm AB is an accurately known non-inductive resistance r_1. The third arm AD consists of a known standard of capacity K_3, whilst the fourth arm DC contains a capacity K_4 in series with a non-inductive resistance R. On applying an alternating voltage to opposite points of the bridge no current will traverse the conjugate arm if the following conditions hold:—

$$K_3 r_1 = K_4 r_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$K_3 r_1 R = K_4 r_2 R = L. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

These conditions are independent of frequency, and therefore apply whatever the wave-form of the applied voltage.

The double adjustment required for balance is of the satisfactory type where the attainment of one condition remains undisturbed in the process of attaining the second. Let us suppose K_3, K_4, and r_1 to be chosen. The procedure consists in first altering r_2 until the effect in the detecting instrument is reduced to a minimum: R is then altered until the zero minimum is indicated. On repeating the process, slightly readjusting r_2 to its best value and then R, the true balance is quickly reached. The value of the inductance required is then given by the formula $L=K_3 r_1 R$.

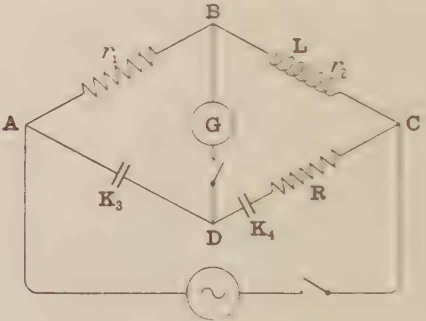


Fig. 1.—Diagram of Bridge.

It will be observed that L is proportional to R. This leads to a result of great practical convenience, namely, the possibility of attaining a balance whatever the value of L may be. Having satisfied the first condition, one is assured beforehand that the second condition can be fulfilled. For the same reason, as will be shown later, it is possible to correct experimentally for any error due to residual inductance or capacity in the bridge.

3. *Proof of Formula.*—The formula is most readily obtained by aid of the theorem that for zero current in the galvanometer or detector the vector-impedances of branches one and two must be in the same proportion as those of branches three and four. This gives

$$\frac{r_1}{r_2+jpL}=\frac{-j/pK_3}{R-j/pK_4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $j=\sqrt{-1}$ and $p=2\pi\times$ frequency. Multiplying across and equating real terms to real, and imaginary to imaginary. we find

$$\frac{r_1}{pK_4}=\frac{r_2}{pK_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1')$$

and

$$Rr_1=\frac{L}{K_3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2')$$

which are identical with equations (1) and (2).

The bridge also lends itself to a simple graphical treatment. In Fig. 2 *ac* and *a′c′* are vectors representing the voltage at any instant between A and C. The voltages across r_1, r_2, and L are represented by *ab*, *be*, and *ec* respectively, the angle *aec*, being a right angle. Similarly the voltages across K_3, K_4 and R are represented by the vectors *a′d*, *de′* and *e′c′* respectively *a′e′c′* being a right angle. For zero current in the galvanometer the voltage from B to D must be zero at every instant. This requires the voltages from A to B and from A to D to be equal both in magnitude and in phase; that is, the triangles *ace* and *a′c′e′* must be similar and equal and *b* must divide *ae* in the same proportion as *d* divides *a′e′*. Denoting the current along the path ABC by *i*, and that along ADC by *i′*, the above conditions are

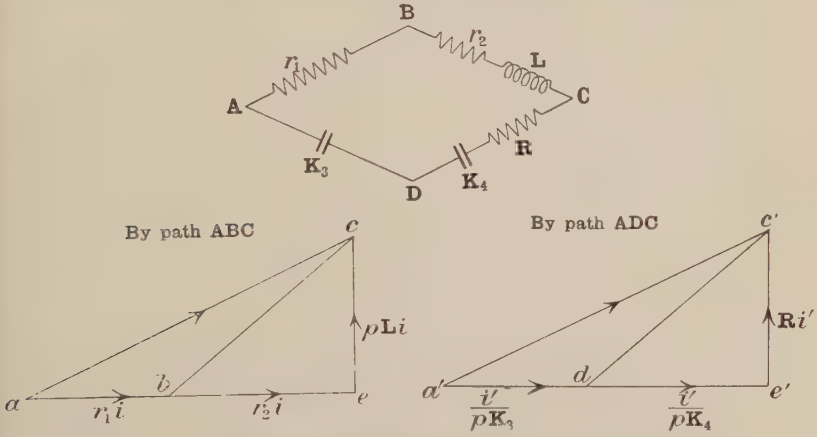


FIG. 2.—VECTORIAL REPRESENTATION OF VOLTAGES IN BRIDGE.

$$\left.\begin{aligned} r_1 i&=\frac{i'}{pK_3}\\ r_2 i&=\frac{i'}{pK_4}\\ Lpi&=Ri' \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or
$$pK_3r_1 = pK_4r_2 = \frac{pL}{R} = \frac{i'}{i} \quad \ldots \ldots \quad (4')$$

leading as before to

$$K_3r_1 = K_4r_2 = \frac{L}{R}.$$

We may regard the path ABC as a resistance in series with an inductance, and the path ADC as a capacity in series with a resistance. The first-named resistance is split at B, the capacity at D, in the proportions required for equal potentials at each instant at the points B and D.

4. It is of interest to consider the relation of the above bridge to a more symmetrical arrangement of inductances, resistances and capacities.

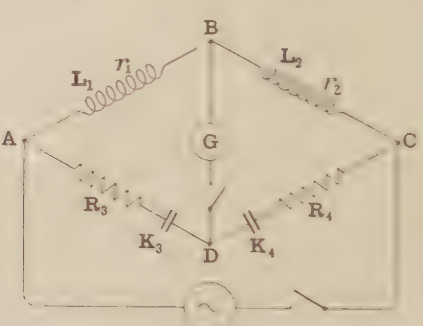


Fig. 3.—Generalised Series-Resistance Bridge.

The bridge of Fig. 3 may be described as of the "series-resistance" type. The conditions for zero current in the arm BD at each instant are

$$\left.\begin{aligned} r_1R_4 - r_2R_3 &= \frac{L_2}{K_3} - \frac{L_1}{K_4} \\ p^2(L_1R_4 - L_2R_3) &= \frac{r_1}{K_4} - \frac{r_2}{K_3} \end{aligned}\right\} \quad \ldots \ldots \quad (5)$$

This bridge has been employed by Rosa[*] and Grover for the measurement of the power-factor of a condenser, the required difference of phase angle of the two condensers being determinable in terms of the known and adjustable inductances L_1 and L_2. We can, however, eliminate the terms in p^2 by writing

---

[*] Bulletin, Bureau of Standards, Vol. III., 1907, p. 390.

$L_1=0$, $R_3=0$ (or $L_2=0$, $R_4=0$), when the above equations reduce to

$$\left.\begin{aligned} r_1R_4&=\frac{L_2}{K_3} \\ \text{and}\qquad \frac{r_1}{K_4}&=\frac{r_2}{K_3} \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

and we have a bridge adapted to the measurement of self-induction. This is the bridge described in the present Paper.

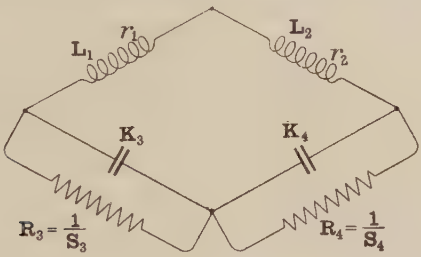


FIG. 4.—GENERALISED SHUNT-RESISTANCE BRIDGE.

If as starting point we take the arrangement in Fig. 4, a bridge of the "shunt-resistance" type, the conditions for zero current in G are

$$\left.\begin{aligned} r_2S_4-r_1S_3+p^2(K_3L_1-K_4L_2)&=0 \\ (K_4r_2-K_3r_1)+(L_2S_4-L_1S_3)\quad&=0 \end{aligned}\right\}. \quad . \; . \; . \; . \quad (7)$$

Once more the conditions for balance are complicated, and involve the frequency. The frequency terms may here be made to vanish by making K_4 and L_1 (or K_3 and L_2) equal to zero, when the conditions of balance reduce to

$$\left.\begin{aligned} r_2S_4-r_1S_3&=0 \\ L_2S_4-K_3r_1&=0 \end{aligned}\right\} \text{ or } \left.\begin{aligned} \frac{r_1}{r_2}&=\frac{R_3}{R_4} \\ L_2&=K_3r_1R_4 \end{aligned}\right\}. \quad . \; . \; . \; . \quad (8)$$

This is the Maxwell bridge. This bridge, as is well known, has the disadvantage that the two adjustments for balance specified in (8) are not independent. The modifications suggested by Rimington and by Niven have the drawback, when employed with alternating currents, of requiring a knowledge of the frequency; the formulæ, moreover, becomes rather complicated and inconvenient in use. In Anderson's well-known modification, operated with alternating current as was first done by Fleming, the two conditions of balance are made independent without sacrificing the advantage of independence of frequency.

5. *Elimination of Residual Inductance and Absorption Effects.*—It is necessary to proceed to a closer examination of the series bridge, with a view to estimating the influence of residual effects on the accuracy of the inductance determination. These residual effects are (1) the inductances l_1 of the coil r_1, l_2 of the arm r_2 (exclusive of that of the coil under test), l_3 in the leads to K_3, and l_4 in the coils R; and (2) absorption in the condensers in the arms three and four, which may be represented by resistances ρ_3 and ρ_4 in series with the capacities K_3 and K_4. In place of equation (3) we have now to write

$$\frac{r_1+jpl_1}{r_2+jp(L+l_2)}=\frac{\rho_3-\frac{j}{pK_3}+jpl_3}{R+\rho_4-\frac{j}{pK_4}+jpl_4} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

leading to the following as the two conditions of balance :—

$$\frac{r_1}{K_4}=\frac{r_2}{K_3}+p^2l_1(R+\rho_4)+p^2l_4r_1-p^2(L+l_2)\rho_3-p^2l_3r_2 \quad . \quad . \quad . \quad (10)$$

and

$$K_3r_1R=L+l_2+K_3(\rho_3r_2-\rho_4r_1)-\frac{K_3}{K_4}\cdot l_1+p^2K_3l_1l_4$$
$$-p^2K_3l_3(L+l_2) \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The procedure for balance remains as before—namely, the adjustment of r_2, followed by that of R. One effect of the terms in p^2 is to diminish the value of r_2 to a slight extent. This is no disadvantage, since r_2 does not enter into the evaluation of L, and therefore need not be known. The second effect of the residual terms is equivalent to an addition to L, which is completely eliminated by repeating the experiment with L removed. Let R_0 denote the resistance in series with K_4 which is required for balance with L cut out, and r_2' and l_2' the new values of r_2 and l_2. Then,

$$K_3r_1R_0=l_2'+K_3(r_2'\rho_3-r_1\rho_4)-\frac{K_3}{K_4}\cdot l_1+p^2K_3l_1l_4'-p^2K_3l_2'l_3 \quad (11')$$

Subtracting (11′) from (11) we have

$$K_3r_1(R-R_0)=L+(l_2-l_2')+K_3\rho_3(r_2-r_2')+p^2K_3l_1(l_4-l_4')$$
$$-p^2K_3l_3(L+l_2-l_2') \quad . \quad . \quad . \quad (12)$$

Calculation shows that the only term (after the first) on the right-hand side of (12) that is of sensible value is (l_2-l_2'); so that we may write

$$K_3r_1(R-R_0)=L+(l_2-l_2') \quad . \quad . \quad . \quad (12')$$

Now the ratio of (l_2-l_2') to L is the ratio of the time-constant of the substituted resistance coils to that of the coil under test. Taking the time-constant of the former as 10^{-8}, the error involved in neglecting (l_2-l_2') will be less than 1 in 10,000 in the case of all inductive coils whose time constant exceeds 10^{-4}; and even if coils be included for which the time-constant is as low as 10^{-5} the error is below 1 in 1,000. We may conclude that it is only rarely that it is necessary to consider the inductance of the substituted resistance coils. Our working formula thus becomes

$$\mathbf{L}=\mathbf{K}_3\boldsymbol{r}_1(\mathbf{R}-\mathbf{R}_0). \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Examples quoted below show that, using standard mica condensers and the usual resistance boxes, the value of R_0 is very small compared with R, except where L is very small, in which case it becomes quite important to obtain the auxiliary balance with L omitted.

It appears from the above examination that by the aid of (13) self-inductance may be determined free from error due either to residual inductance in the resistance coils used, or to absorption in the condensers.

In regard to the term (l_2-l_2') in (12′) it may be observed that the difficulty of making allowance for it is common to all bridge methods of measuring inductance.

6. *Sensitiveness of the Bridge.*—If a pure sine voltage, v, be applied between the points A and C of the bridge (Fig. 1), the current through the galvanometer arm BD is given by the expression

$$i_g=\frac{v}{A^2+B^2}\left\{A\left(\frac{L}{K_3}-r_1R\right)+B\left(\frac{r_1}{pK_4}-\frac{r_2}{pK_3}\right)-j\left[B\left(\frac{L}{K_3}-r_1R\right)\right.\right.$$
$$\left.\left.-A\left(\frac{r_1}{pK_4}-\frac{r_2}{pK_3}\right)\right]\right\}, \quad . \quad . \quad (14)$$

where

$$A\equiv R(r_1g+r_1r_2+r_2g)-\frac{r_1+r_2}{p^2K_3K_4}+L\left(\frac{r_1+g}{K_4}+\frac{R+r_1+g}{K_3}\right), \quad . \quad (15)$$

and

$$B\equiv pLR(r_1+g)-\frac{pL}{p^2K_3K_4}-\frac{r_1g+r_1r_2+r_2g}{pK_3}-\frac{(g+r)(r_1+r_2)+r_1r_2}{pK_4} \quad (16)$$

The arm BD is assumed to consist of a pure resistance g; that is, inductance and back E.M.F. in the detector are neglected.

As A and B occur to the first power in the numerator of (14), but to the second power in the denominator, the current i_g for a given voltage across the bridge will be increased by reducing A and B. The expressions for A and B involve the frequency, and it appears that when $p=0$ both quantities become infinite. The bridge is thus inapplicable to steady currents. As p increases A becomes zero at a certain frequency, then increasing numerically, but with change of sign. B, like A, has the value minus infinity at zero frequency, and passes through zero at a certain frequency, generally higher than that at which A vanishes. There is, therefore, some intermediate value of the frequency for which the sensitivity of the bridge is a maximum. This value depends on the capacities employed and on the inductance to be measured. The expressions for A and B are made up of products of resistances and reactances taken three at a time, and the general rule for high sensibility is to aim at making the resistances and reactances of the arms and of the detecting instrument of approximately the same value. Using capacities each equal to $\frac{1}{3}$ m.f it would appear that the best frequency to select in the case of inductances of the order of a tenth of a henry is about 200 per second, higher frequencies being called for the lower the inductance.

Much, however, will depend on the choice of detecting instrument. The vibration galvanometer appears to have its greatest sensitivity at low frequencies, say, 100 per second; whilst the telephone (or rather the ear) has its maximum sensitivity at 800 or 1,000∼. The sensibility of the Sumpner alternate-current galvanometer is independent of frequency, provided the voltage applied to the field-coil is in proportion to the frequency. The fact that both the sensitivity of the bridge and that of the ear rise with frequency are to the advantage of the choice of the telephone, and in practice it has been found that, at all events over the lower range of inductance, the superiority as regards accuracy rests distinctly with that instrument.

From (14) it may be seen that the galvanometer current is made up of two components in quadrature; one arising from the non-attainment of the condition $L=K_3r_1R$, the other from the non-attainment of the second condition $\frac{r_1}{K_4}=\frac{r_2}{K_3}$. This result applies indeed to all bridges involving two conditions of balance.

6. *Effects of Frequency.*—Apart from the slight residual effects depending on frequency, which have already been discussed, there are three effects of frequency which may affect the value of inductance obtained by an alternating-current method. These are the skin effect (both on the inductance of the coil under test and on the resistance of the bridge coils), the effect of frequency on the capacity of a mica condenser, and, lastly, the effect arising from distributed capacity in the coil under test.

At frequencies below, say, 2,000 per second the first of them, the skin effect, is inappreciable.

The second effect is appreciable in measurements where the highest accuracy is required. A standard mica condenser shows a decrease of capacity of it may be five parts in 10,000 when the frequency rises from 100 to 500 per second. It is thus necessary that the capacity of the condenser should be known at the frequency used in the test.

The effect of distributed capacity is to cause an increase in the effective inductance of the coil tested, the increase being proportional to the value of the inductance and to the square of the frequency. The effect is only of importance in the case of large inductances and at the higher frequencies, and where necessary its value can always be experimentally determined (see, for example, observations Nos. 14 and 15 below).

7. *Experimental Arrangements and Results.*—Examples of tests are included for inductances ranging from 0·4717 henry to 2·05 microhenries. The whole range may be covered without change in the pair of condensers employed. As a rule two nominal $\frac{1}{3}$ m.f. mica standard condensers were used. The value of r_1 was 1, 10, 20, 100, or 200 ohms. To obtain the exact adjustment of r_2 and R for balance, bridge wires were inserted in the arms BC and CD. Each of these consisted of a length of about 80 cms. of constantan wire doubled on itself, the two halves running parallel at about 0·5 cm. apart, the whole being mounted on a baseboard graduated in centimetres. A short-circuiting sliding bridge-piece allows of a continuous variation of resistance. The resistance per centimetre of wire was almost exactly 0·02 ohm. With their help exact balance could be rapidly and accurately secured, the value of R being thus determinable to within a hundredth of an ohm.

In the case of very low inductances of only a few microhenries, it is necessary to allow for the small alteration of inductance in the bridge-wire in the arm BC between the settings for R and R_0; in other words, equation (12′) should be employed for the calculation and not (13). A continuous variation of resistance with practically constant inductance may, however, be secured by the aid of the mercury U-tube of Wenner and Dellinger, or by using a carbon plate rheostat. The latter method was used in some of the measurements recorded below, the bridge wire in arm two being dispensed with.

The *sources of current* employed were a small induction coil or buzzer giving a frequency of 95, another giving 530; a small transformer with tuning fork interrupter of 100 ∾, which provided a source of very steady frequency for use with the vibration galvanometer; also a microphonic hummer giving 512∾.

With regard to *detecting instruments*: Except in the case of the largest inductances, and of coils containing iron, the telephone in conjunction with the buzzer of 530 ∾ was found to give very satisfactory results. Theoretically, owing to effects of residual inductance and of absorption, it is impossible to obtain perfect silence in the telephone unless a pure tone is employed. In practice this difficulty largely disappears. With low inductances, say, below 0·1 millihenry, the effect of overtones is almost inappreciable. At higher values it is easy after a little practice to reduce the fundamental note in the telephone to inaudibility in spite of the distinct presence of the overtones. Using a frequency as high as 530 for the fundamental tone this is particularly the case: probably only the first two, or perhaps three, overtones are effective, for not only is the intensity of the higher components present in the source smaller, but the sensibility of the ear to the corresponding tones is at the same time reduced. Readings are taken of the limiting resistances at each end of the range of inaudibility—these limits are surprisingly sharp—and the mean of these readings gives the true balancing value.

For the largest inductances the vibration galvanometer was used.

For the testing of coils containing iron the telephone is practically useless. With the vibration galvanometer, on the other hand, the condition of zero movement is reached as completely as in the case of air coils, though, of course, the meaning of the resulting figures is not so easy to define.

The standard mica condenser used throughout as K_3 had the value 0·33200 m.f. at 16°C. Its value at other temperatures was read off from the curve of Fig. 5.

The condenser K_4 was a nominal $\frac{1}{3}$ m.f. mica condenser, except in experiment No. 16 (*see* footnote).

In the last column T stands for telephone, and V.G. for vibration galvanometer.

Table I.

No.	K_3(m.f.)	r_1	R	R_0	$L=K_3r_1(R-R_0)$	Estimated error (parts in 10,000).	Detecting instrument and frequency.
Single circular turn of copper wire, diameter of wire 0·071 cm., circumference of circle 150 cm.							
1	0·3318	1·0102	6·49±0·02	0·455	2·04 microhenry	64	T. 530
2	0·3320	1·008	9·72±0·02	3·50	2·08 microhenry	64	T. 530
Helix, single layer of 147 turns, length of helix 22·8 cm., external diameter 5·36 cm., diameter of wire 1·22 mm.							
3	0·33194	10	70·05±0·04	0·67	0·2303 millihenry	6·5	T. 530
4	0·33194	10	70·50±0·06	1·02	0·2306 millihenry	13	T. 95
Helix of ohmic resistance 1·1 ohm, with core of soft iron wires.							
5	0·3319	200	1539·5±0·5	0·2	0·10216 henry	6	V.G. 95
6	0·3319	200	1530·5±0·5	0·2	0·10156 henry	6	V.G. 95
Circular coil of 500 turns, mean diameter 22 cm., resistance 9 ohms.							
7	0·33194	200	1198·39±0·04	0·16	0·079548 henry	0·5	T. 530
8	0·33194	100	2397·42±0·1	0·25	0·079572 henry	0·5	T. 530
9	0·33194	200	1198·4 ±0·4	0·2	0·079540 henry	5	V.G. 95
Equal circular coils A and B, of 500 turns, mean diameter 36 cm., axial breath 2·54 cm. radial depth 5·6 cm. Placed coaxially one over the other in immediate contact.							
A only—							
10	0·33190	200	2362·19±0·4	0·2	0·15679 henry	1·7	V.G. 95
B only—							
11	0·33190	200	2403·5±0·4	0·2	0·15953 henry	1·7	V.G. 95
A and B in series, aiding—							
12	0·33190	200	7094·5±2·5	0·2	0·47090 henry	3·6	V.G. 95
A and B in series opposing—							
13	0·33190	200	2440·4±0·4	0·2	0·16199 henry	1·7	V.G. 95
From (12) and (13) we have and from (10) and (11) we have also from (12 and (13) by subtraction					$L_A+L_B=0·31644$ henry, $L_A+L_B=0·31632$ henry ; $4\ M=0·30891$ henry ; $\therefore\ M=0·07723$ henry		
Coils A and B in series and aiding—							
14	0·33197	200	7104·9±1·5	0·16	0·47170 henry	2·3	T. 530
15	0·33197	200	7090·6±2·0	0·2	0·47074 henry	3·2	V.G. 95
Circular coil of 500 turns, mean diameter 22 cm., resistance 9 ohms.							
16	0·3319	200	1199·55±0·04	0·25	0·07961 henry	—	T.530

Remarks on some of the above observations :—

Nos. 1 and 2.—The inductance calculated from the dimensions of the circular wire is 2·054 microhenries (±0·005). In No. 1 a correction of −0·015 microhenry was applied to allow for the change of inductance due to movement of slider of bridge-wire in arm two (as per equation (12)). In No. 2 a carbon plate rheostat was used to adjust r_2, hence no such correction was required.

Nos. 5 and 6.—Although iron was present within the coil, no difficulty was experienced in obtaining a perfect balance with the vibration galvanometer. The effective resistance of the coil is at the same time ascertained ; in the case of this coil it was 49 ohms. In No. 5 the voltage applied to the bridge was 2·8 volts ; in No. 6 it was 1·7 volts.

Nos. 10 to 13.—These serve as examples of the determination of a mutual inductance.

Nos. 14 and 15.—These are observations on a large inductance, and the measurements at 530 ∼ and 95 ∼ serve for the determination of the distributed capacity. The value of L at 530 ∼ proves greater than at 95 ∼ by 20·4 parts in 10,000. Of these perhaps some 5 parts are accounted for by the diminution of K_3 with frequency. The remaining excess must be assigned to the effect of distributed capacity, as expressed in the formula

$$L_n = L_0(1-4\pi^2 n^2 k L_0),$$

where n denotes the frequency. The value of the distributed capacity k thereby calculated is $3{\cdot}9 \times 10^{-5}$ m.f. At the lower frequency, 95 per second, it appears that the increase in effective inductance due to distributed capacity is below 1 part in 10,000, whilst at 530 ∼ it is some 15 parts in 10,000.

No. 16.—This test differs from No. 7 in that K_4 was an ordinary commercial (Mansbridge) condenser, and not a mica condenser. Owing to the large absorption, balance with L cut out was only possible by inserting a resistance of not less than 30 ohms in series with the standard condenser K_3. The value of R_0 given above corresponds to the series resistance 30 ohms in the arm three. The value of ρ_4 deduced from the data of this balance was 5·16 ohms, K_4 being 1·838 m.f. ; and the power-factor of the condenser works out at 0·031. By comparing Nos. 7 and 16 the error in the result for L, which is introduced by the use of such a highly absorptive condenser, is seen to be less than one part in 1,000. This example shows that it is possible to obtain results sufficiently accurate for many purposes without the use of a mica condenser in the fourth arm of the bridge.

8. *The Measurement of Mutual Inductance.*—Any bridge for the determination of self- will serve for the determination of mutual-inductance. If the coils are put in series the total self-inductance is $L_1+L_2\pm 2M$. Two adjustments of the bridge for balance, the second with connections of the coils reversed, lead to the difference 4M. This method is quite satisfactory where the coefficient of coupling of the coils is not too low. An example is given in Nos. 10 to 13 above.

9. *Standards of Self-Inductance.*—It is obvious that a method for the measurement of inductance in terms of capacity may be reversed. It may be regarded as a means of determining a capacity in terms of a standard of inductance. From the point of view of accuracy and reliability of results the latter may well be regarded as the proper order of procedure. An inductance standard has a very low temperature coefficient, and when

carefully designed and constructed is probably far more constant than a standard mica condenser.

Into the problem of constructing suitable primary standards of self-inductance it is not proposed to enter. It may be pointed out, however, that secondary standards are readily procurable. With the possession of such a standard the capacity of mica condensers can be checked from time to time, and their variation with temperature determined. The results of a test of temperature variation are here included. They afford, incidentally, an example of the erratic changes to which the capacity of a mica condenser is liable.*

10. *A Test of the Temperature-Coefficient of a Mica Condenser.* The measurements were made by the series-resistance bridge, the formula $K=\frac{L}{r_1(R-R_0)}$ being employed. The inductance coil was that used in tests 7 to 9 of Table I.

$r_1=200$ ohms ; $R_0=0{\cdot}15$ ohm. $K_{16}=0{\cdot}33200$ m.f.

R was determined always to within 1 part in 20,000. Temperatures were ascertained to within 0·2°C.

Table II.

Temperature-variation of Capacity of Mica Condenser $v=530$.

No.	1.	2.	3.	4.	5.	6.	7.
Temp. (°C)	18	23·2	28·5	33·2	28·3	24·2	19·3
$R-R_0$ ...	1198·37	1199·17	1200·73	1203·18	1200·68	1199·95	1199·15
Capacity	0·33212	0·33191	0·33153	0·33079	0·33148	0·33169	0·33190
No.	8.	9.	10.	11.	12.	13.	14.
Temp. (C°)	0	10	18·7	25·0	31·0	25·6	19·4
$R-R_0$ ...	1197·25	1198·22	1199·11	1200·19	1202·49	1200·48	1199·16
Capacity	0·33244	0·33217	0·33191	0·33184	0·33163	0·33099	0·33154

From the above figures the graph of Fig. 5 is drawn. By following the numbers appended to the points on the graph it appears that between the observations 5 and 6 a sudden alteration in the capacity occurred, to the extent of 5·4 parts in 10,000. After No. 6 the results are closely expressible as a single-valued function of temperature. The time covered by the tests was 17 days.

---

* *See* Curtis, Bureau of Standards, Washington, November, 1910.

The graph shows how rapidly the temperature-coefficient increases at temperatures above 15°C. Over the range 0°—15°C. the mean coefficient is −0·000080. from 15° to 20° C. it is −0·00010. from 20° to 25° C. −0·00015. and from 25° to 30° C. −0·00036.

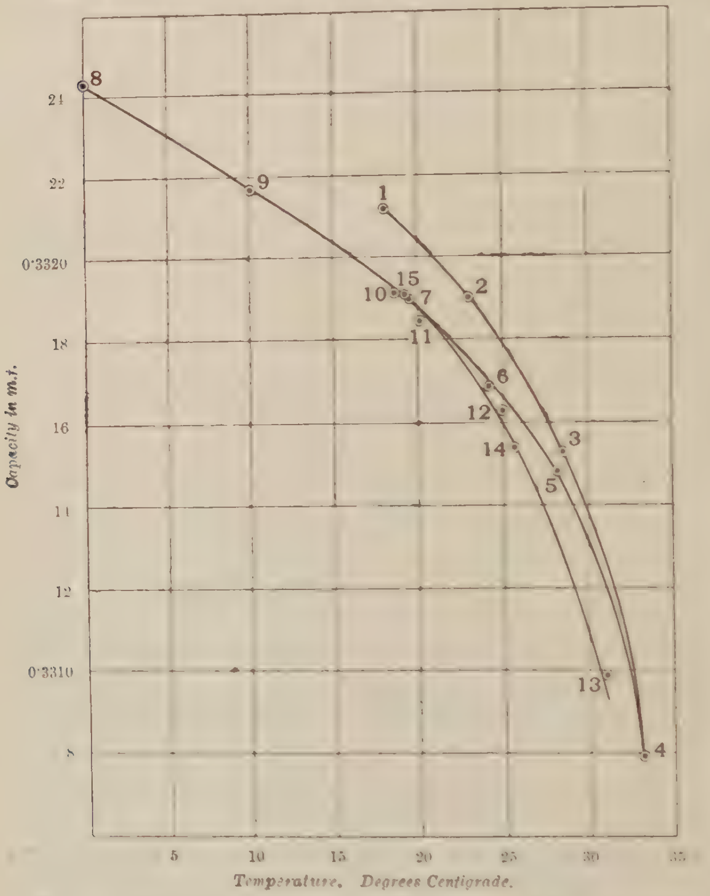


Fig. 5.—Temperature-variation of Capacity of Mica Condenser.

Summary.

1. An alternate-current bridge method is proposed for the determination of self-induction in terms of capacity and

resistance. The inductance L is given by the relation $L=K_3r_1R$; in addition to which it is also necessary for balance of the bridge to satisfy the condition $K_3r_1=K_4r_2$.

2. The two conditions of balance may be secured in practice without mutual interference. The end point is therefore rapidly attained. The possibility of effecting a balance is unlimited by the value of the unknown L.

3. The method is independent of frequency. This has the accompanying advantage that it is unnecessary to employ a pure sine voltage. Very good results may be attained with a buzzer as source and a telephone receiver as detector, at, say, 500 ∾.

4. The dependence of sensibility of the bridge on the frequency is discussed, and it is shown that over a wide range (say, 100 ∾ to 1,000 ∾) the sensibility is high.

5. The effects of residual inductance in the resistance coils and leads, and of absorption in the condensers, may be simply and correctly allowed for, the formula then becoming

$$L=K_3r_1(R-R_0).$$

This fact is of especial importance in the accurate determination of very small inductances.

6. Tests are quoted showing that with the same pair of condensers measurements over the full range from one microhenry upwards may be made. For inductances of the order of 10 microhenries the error may be kept within a few parts in 1,000; whilst if the inductance is as high as a few millihenries the error of any measurement may be reduced below one part in 10,000.

7. The application of this bridge to the determination of capacity in terms of self-inductance is discussed, and an example is given of a test of the temperature variation of capacity of a standard mica condenser over the range 0°—30°C.

ABSTRACT.

1. An alternate-current bridge method is proposed for the determination of self-induction in terms of capacity and resistance. The inductance L is given by the relation $L=K_3r_1R$; in addition to which it is also necessary for balance of the bridge to satisfy the condition $K_3r_1=K_4r_2$.

2. The two conditions of balance may be secured in practice without mutual interference. The end point is therefore rapidly attained.

The possibility of effecting a balance is unlimited by the value of the unknown L.

3. The method is independent of frequency. This has the accompanying advantage that it is unnecessary to employ a pure sine voltage. Very good results may be attained with a buzzer as source and a telephone receiver as detector, at, say, 500∼.

4. The dependence of sensibility of the bridge on the frequency is discussed, and it is shown that over a wide range (say, 100∼ to 1,000∼) the sensibility is high.

5. The effects of residual inductance in the resistance coils and leads, and of absorption in the condensers, may be simply and correctly allowed for, the formula then becoming

$$L=K_3 r_1(R-R_0).$$

This fact is of especial importance in the accurate determination of very small inductances.

6. Tests are quoted showing that with the same pair of condensers measurements over the full range from one microhenry upwards may be made. For inductances of the order of 10 microhenries the error may be kept within a few parts in 1,000; whilst if the inductance is as high as a few millihenries the error of any measurement may be reduced below one part in 10,000.

7. The application of this bridge to the determination of capacity in terms of self-inductance is discussed, and an example is given of a test of the temperature variation of capacity of a standard mica condenser over the range 0°—30°C.

DISCUSSION.

Mr. A. CAMPBELL congratulated the author on his clear treatment of the general case. His method had several advantages, the most important of which was that he took a zero reading to eliminate the inductance of the leads by substituting a non-inductive resistance for the inductance to be measured. There is, of course, a difficulty in all such methods in obtaining a non-inductive resistance, but this can be got over by using a small inductance of which the value can be calculated, such as a pair of parallel wires. He could not say how far the terms in equation 12 could always be neglected as done by the author with frequencies greater than 1,000. Particular cases could be tried to see how far this was permissible. Among the disadvantages, he instanced the use of standard condensers in place of standard inductances. The latter could be obtained at less cost and of greater accuracy than condensers. Moreover, the values of condensers varied more rapidly with temperature and frequency than did those of inductances. The former defect was aggravated by the time required for a condenser to take up a steady temperature. The usual practice was to keep it at a given temperature for 24 hours or more in measuring to tenths or hundredths per cent. Another difficulty in bridge work with condensers is caused by earth capacities. If the point of earthing be altered different results may be obtained. He suggested that the galvanometer and battery might profitably be interchanged. The position described in the Paper was the worst for disturbances due to earth capacities.

Mr. F. E. SMITH mentioned that in Rosa and Grover's Paper, quoted by the author, a figure practically identical with Fig. 3 in Mr. Owen's Paper appeared. Some of the equations, also, were very similar, but Rosa and Grover had, apparently, overlooked the fact that by making one of the R's and one of the L's zero the bridge could be used for the measurement of self-induction. He was surprised that Mr. Owen appeared to prefer the telephone to the vibration galvanometer in many cases. He would have expected the latter to give more satisfaction in almost all cases. With regard to the discrepancy found by the author in the temperature curve for his condenser, he might say that in the case of paraffin wax condensers it was always dangerous to cool to 0 deg., as a change occurred in the wax which introduced trouble. He had gone into the matter of changes in the resistance of the old B.A. resistance coils when cooled to 0 deg., and had shown that these were due to changes in the wax.

Dr. **Russell** said that he had used Mr. Owen's method of measuring inductance in his laboratory and had found it simple, accurate and most satisfactory. When ordinary alternating-current supply was available good results were obtained either with a telephone or a vibration galvanometer. The theorem on which the method is based is extremely interesting from the theoretical point of view, and several curious results follow from it. Mr. Owen's method of proof was well adapted to the needs of electrotechnical students, but he preferred the analytical methods as they were more rigorous.

The **Author**, in reply, referred to the variation of capacity with frequency. This was most marked at low frequencies, and as, to get sensibility, the bridge had to be used at frequencies of 100 or more, one was working outside the most dangerous region. With regard to the temperature variations, he pointed out that the condenser could always be tested against a standard inductance if need be. In the test of temperature-coefficient he had allowed the condenser to stand for four hours after the required temperature had been reached; the time to be allowed to attain the temperature of the bath could be calculated from the fact that the condenser was found to require 1¼ hours to cover half the impressed interval of temperature. In ordinary use, as the daily range was not more than 3° or 4°C., and as 1° only introduced an error of 1 in 10,000, he thought the trouble would be inappreciable. He had tried both positions of the galvanometer and battery, and sometimes one and sometimes the other proved most satisfactory. The difficulty about earth capacities was one that had to be guarded against in all balanced bridge methods when the utmost accuracy was required. The effect was likely to be very small in the bridge described, since the capacities employed were comparatively great.

IV. *On the Coefficient of Diffusion in Dilute Solutions. By* BASIL W. CLACK, *B.Sc., Lecturer in Physics at Birkbeck College.*

RECEIVED SEPTEMBER 29, 1914.

§ 1. Introduction.
§ 2. Modifications in the Apparatus.
§ 3. The Apparatus.
§ 4. Results.
§ 5. Diffusivity at a definite concentration.
§ 6. The end-correction.
§ 7. Effect of the diffused salt.
§ 8. Effect of the material of the tank.
§ 9. Discussion of results.

§ 1. *Introduction.*

THE author has been interested for a number of years in the investigation of the phenomena of the diffusion of salts through water, using for the purpose special flasks filled with the solution under examination, one suspended from each arm of a delicate balance, in a large bath of distilled water maintained at various constant temperatures in a thermostat room. Each flask was fitted with a vertical tube through which the salt diffused upwards and the design of the flask was such as to maintain the concentration of the solution constant at each end of the tube. The diffusion tubes of both flasks were of equal length, but their cross-sections differed considerably. A method of differential weighing was used to eliminate errors due to small changes in the density of the bath, and from the final steady rate at which the flasks changed in weight as the salt diffused out, the value of the coefficient of diffusion of the salts can be deduced.*

The objects of the present Paper are :—

1. To describe improvements made in the apparatus by means of which the results can be obtained more quickly.

2. To investigate the diffusion of certain salts down to very dilute solutions at a constant temperature.

---

* *See* Clack, "Proc." Ph. Soc., XXI., p. 863, 1908; XXIV., p. 40, 1911.

§ 2. *Modifications in the Apparatus.*

The apparatus already employed possessed the disadvantage that much time was wasted before the rate of change in weight of the flasks became approximately constant, six or seven days being required, and attempts were made to hasten the time of attainment of the steady state. In the discussion [" Proc." Ph. Soc., p. 49, 1911] Mrs. Griffiths (Miss C. H. Knowles) showed that the steady state would be hastened by filling the diffusion tubes to half their height with the solution under investigation, the rest of the tubes containing pure water. This method was tested in a number of experiments but with hardly the success expected. Not only was the steady state not accelerated very much, but the filling of the tubes seemed to produce too much disturbance, and the results obtained were not as consistent as desired. With specially careful manipulation the method might prove more successful, but in the present Paper an alternative means of hastening the steady state has been adopted, that of reducing the length of the diffusion tubes, and the arrangement at present employed is so satisfactory that the steady state is obtained almost at once. A result differing in most cases by only 1 or 2 per cent. from its final value is obtained in one day, enabling very rapid determinations of the value of the coefficient of diffusion to be made.

That shortening the diffusion tube should hasten the attainment of the steady state is well known. The case in which the liquid is moving with an impressed velocity was investigated theoretically in a note published by Miss A. Somers (" Proc." Ph. Soc., XXV., p. 74, 1912), and the present author studied the matter in 1908 in the Paper previously mentioned, by experiments on diffusion employing tubes 4 cm., 2 cm. and 1 cm. long (*see* also " Phil. Mag.," Vol. XVI., Plate XXV., Fig. 6, 1908). In this work it was observed that the end-correction to the length of the tube, which was negligible in the longest tube, because important as the length was reduced, and to avoid the error involved it has been found necessary to reduce not only the length, but also the diameter of the tubes, a battery of short and narrow tubes replacing the single wide tube previously employed. This idea was proposed by the author in 1908, in the Paper referred to, but as the same suggestion was made by Dr. Griffiths and by Prof. Lees in the discussion following the Paper read in 1911, his attention was again directed to it.

The general shape of the curves obtained by plotting the change in weight of the flasks against the time is shown in the annexed family of curves (Fig. 1) dealing with solutions of KCl of the various concentrations indicated. A comparison of these curves with those already published will show how great has been the saving of time, an experiment which previously required 21 days, being now completed in less than a week.

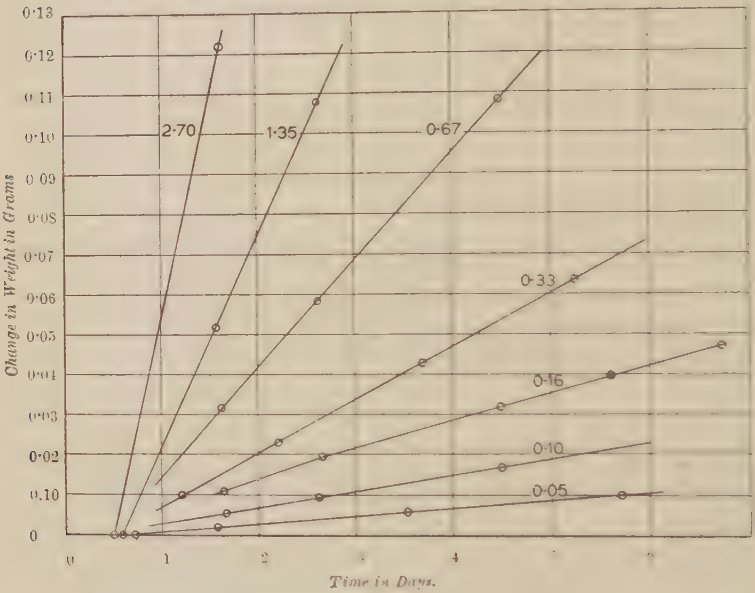


FIG. 1.

§ 3. *The Apparatus.*

The general arrangement of the apparatus and the method of using it, is similar to that already described in the "Proc." Ph. Soc., December, 1911, and need not be repeated here. The aperture in each flask was closed by a glass plate drilled to receive the diffusion tubes, which were sealed in position by canada balsam.

With a battery of four parallel vertical tubes, each about 2 cm. long and 0·448 sq. cm. in area, fitted into the diffusion flask on one side of the balance and a single similar tube fitted into the other, the amount of salt diffusing was sufficient to make accurate weighings possible.

The dimensions of the tubes, found in the manner previously described, are given in the following table :—

Length.	Area.
$1{\cdot}997_6$ cm. $= L_2$	$0{\cdot}445_1$ sq. cm. $= A_2$
$2{\cdot}000_3$	$0{\cdot}454_8$
$1{\cdot}998_9$	$0{\cdot}451_5$
$2{\cdot}000_0$	$0{\cdot}440_7$
$1{\cdot}999_7$	$0{\cdot}447_4$
Mean $2{\cdot}000$ cm. $= L_1$	*Total* $= 1{\cdot}794_4$ sq. cm. $= A_1$

Results obtained with this apparatus are distinguished by the letter β in the following tables.

§ 4. *Results.*

The results for solutions of potassium chloride, potassium nitrate and sodium chloride at constant temperatures, all in the near neighbourhood of 19°C., are tabulated below. For purposes of comparison some results have been included, obtained by means of the apparatus described in 1911. These are distinguished by the letter α.

The value of the diffusivity in C.G.S. units is obtained from the formula proved in the earlier Paper.

$$K = \frac{L_1 L_2 (i_1 - i_2)}{(A_1 L_2 - A_2 L_1) N \{1 - \frac{1}{2} N \delta (D - N)\} \{1 - \delta (D - N)\}} \quad . \quad \text{(i.)}$$

where L_1 and L_2 = lengths of the diffusion tubes fitted into the two flasks.

A_1 and A_2 = their total areas of cross-section.

N = concentration of the solution in gms. per cc. of the solution at the lower end of the tubes.

D = density of the solution at the same point.

i_1 and i_2 = final steady change in weight of the two diffusion flasks per second. The balance records $(i_1 - i_2)$.

δ = ratio of the increase in volume produced to the increase in mass of salt dissolved, for a solution of concentration N.

Results to which no number is attached in the last column of the table are obtained by interpolation from the results published in the earlier Papers of the author.

KCl.

Normality.	N in gms. per cc.	Temp. in °C.	Mean slope $(i_1-i_2) \times 10^7$.	$K \times 10^5$.	Apparatus.	Experiment No.
2·70	0·2	18·5	...	1·517	α	...
		18·8	5·302	1·526	α	28
		18·7	12·38	1·550	β	10
		18·8	12·26	1·558	β	11
1·35	0·1	18·5	...	1·538	α	...
		18·6	6·124	1·496	β	8
		18·7	6·156	1·495	β	9
0·67	0·05	18·5	1·417	1·524	α	7
		18·4	1·325	1·436	α	15
		18·6	3·035	1·457	β	6
		18·9	3·130	1·473	β	12
		18·7	3·091	1·475	β	14
0·33	0·025	18·6	1·581	1·464	β	16
		18·7	1·564	1·420	β	17
0·165	0·0125	18·5	0·787	1·458	β	18
		18·6	0·745	1·380	β	19
		18·7	0·783	1·450	β	29
0·10	0·0075	18·3	0·447	1·360	β	20
		18·7	0·448	1·363	β	21
0·05	0·0037	18·3	0·228	1·366	β	22
		18·1	0·234	1·405	β	23
0·03	0·0020	17·9	0·133	1·304	β	24
		18·4	0·136	1·334	β	25

KNO_3.

Normality.	N in gms. per cc.	Temp. in °C.	Mean slope $(i_1-i_2) \times 10^7$.	$K \times 10^5$.	Apparatus.	Experiment No.
1·0	0·1	18·5	...	1·319	α	...
		18·8	5·289	1·290	β	30
		19·0	5·027	1·316	β	31
0·5	0·05	18·5	...	1·333	α	...
		18·3	2·784	1·340	β	42
		19·1	2·930	1·411	β	32
		19·2	2·872	1·388	β	33
0·25	0·025	19·2	1·479	1·399	β	34
		19·2	1·555	1·408	β	35
0·10	0·010	19·1	0·620	1·454	β	36
		19·2	0·622	1·458	β	37
0·05	0·005	19·0	0·343	1·547	β	38
		18·8	0·332	1·513	β	39
0·02	0·002	18·6	0·135	1·489	β	40
		18·5	0·131	1·454	β	41

NaCl.

Normality.	N in gms. per cc.	Temp. in °C.	Mean slope $(i_1 - i_2) \times 10^7$.	$K \times 10^5$.	Apparatus.	Experiment No.
3·40	0·2	18·5	10·10	1·228	β	45
		18·4	10·17	1·233	β	46
1·72	0·1	18·7	5·290	1·215	β	47
		18·7	5·213	1·198	β	48
0·85	0·05	18·5	2·977	1·200	β	49
		18·6	2·738	1·175	β	50
0·34	0·02	19·0	1·077	1·148	β	51
		18·9	1·109	1·193	β	52
0·034	0·002	19·0	0·118	1·164	β	53

The value of the coefficient of diffusion varies to some extent with the concentration of the solution, and the results here calculated give the value of what may be called the "mean diffusivity" for the solution in the diffusion tube, that is for a solution varying in concentration from zero to a maximum of

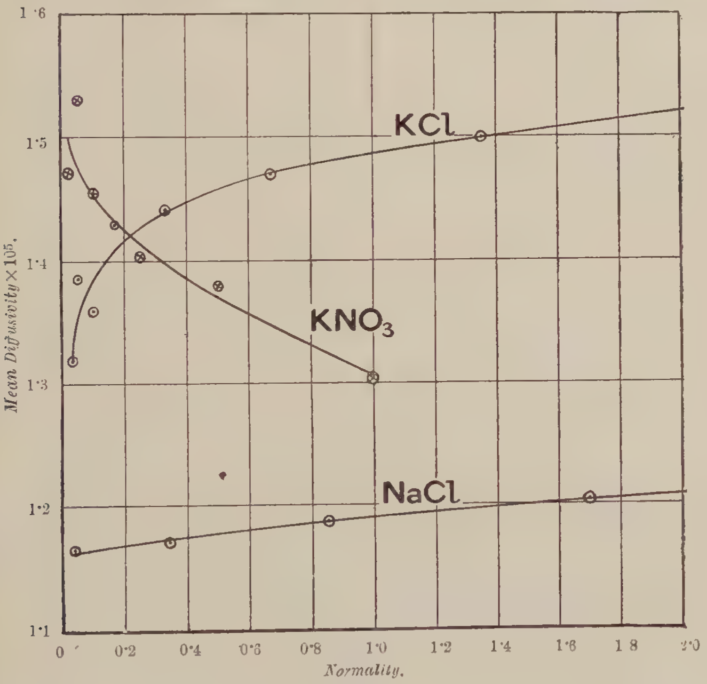


FIG. 2.

N in each experiment. The results are shown graphically in the accompanying curves (Fig. 2), in which the value of the mean diffusivity, K, is plotted against the maximum concentration, N, of the solution employed in each of the experiments.

§ 5. *Diffusivity at a Definite Concentration.*

A difficulty is encountered in attempting to find the exact value of the coefficient of diffusion at a *definite concentration* from the observations recorded in this Paper, due to the velocity with which the solution is moving down the tube. This velocity is caused by the change in volume of the solution as it becomes less concentrated by diffusion; it not only varies with the strength of the solution employed in the separate experiments, but it differs slightly at different points in the diffusion tube in the same experiment.

This movement makes the exact solution of the problem very difficult, if not impossible; but it is comparatively easy to develop a formula for the coefficient of diffusion at a definite concentration, which is likely to give results as accurate as the observations justify, if the velocity is so small that it can be neglected altogether, and the liquid considered to be at rest.

It has already been shown ("Proc." Ph. Soc. XXI., p. 863, 1908) that the velocity is of the order

$$\{i\delta(D-N)\} / \{1-\delta(D-N)\},$$

and by introducing the values of these quantities, as found by actual experiment, the velocity in the experiments of the present research is proved in all cases to be very small, the average value being of the order 10^{-7} cm. per sec., *i.e.*, about 1 cm. in four months.

This movement produces a measurable effect in the rate of change in the weight of the flasks, and has been studied in the previous Papers published by the author, where it is shown that the corrections, to allow for the movement of the water, introduce the factors $\{1-\frac{1}{2}N\delta(D-N)\}/\{1-\delta(D-N)\}$ into the calculation of the value of the coefficient of diffusion by equation (i.); yet it has only a small influence on the quantity of salt transmitted through the diffusion tubes—4 per cent. in the extreme case.

Since the effect of the velocity of the water has been taken into account in arriving at Equation (i.), it seems certain that the value of the coefficient of diffusion between given limits of concentration, as calculated by this equation from the experiments described in this Paper, cannot differ seriously from that value which would be obtained between the same limits of concentration were it possible to work with a perfectly stationary column of a salt solution.

Consider, then, a diffusion tube of unit cross-section so arranged that its upper end is maintained in contact with pure water and that the lower end is continually in contact with salt solution of a constant concentration, and assume that no movement takes place in the water in the tube. When diffusion has reached the steady state let n be the concentration of the solution in the tube at a distance l cm. from its upper end.

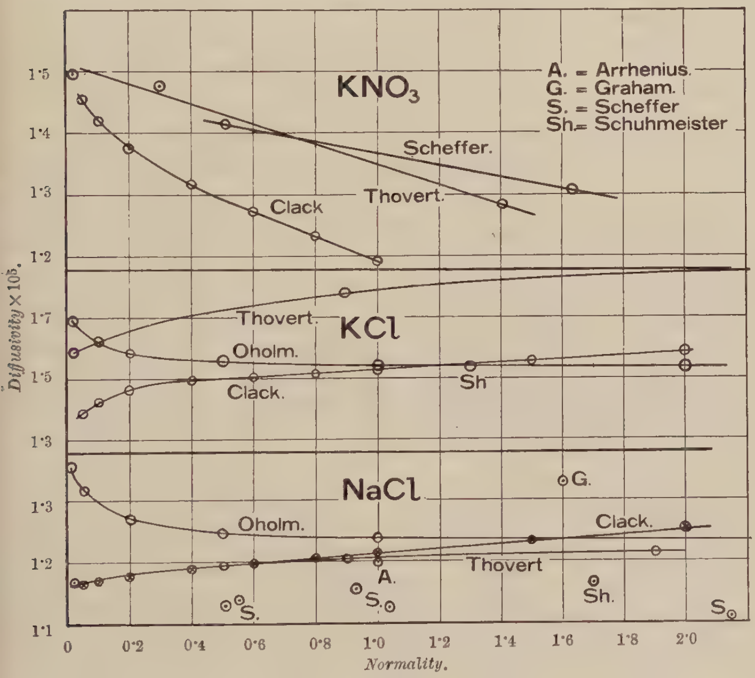


FIG. 3.

Let C = constant quantity of salt transmitted per second.

${}_0K_n$ = coefficient of diffusion of the solution, varying in concentration between the limits zero and n, which satisfies the equation $C = {}_0K_n n/l$.

K_n = actual value of the coefficient of diffusion of the solution at the concentration n.

As already explained, it is assumed that the value of ${}_0K_n$ may be taken with sufficient accuracy as that obtained experimentally in this research.

Then $${}_0K_n\, n/l = K_n\, dn/dl = C,$$

i.e., $$K_n = C\, dl/dn.$$

Now $$Cl = {}_0K_n \times n$$

$$\therefore\quad C\, dl/dn = {}_0K_n + n \times d/dn({}_0K_n)$$

i.e. $$K_n = {}_0K_n + n \times d/dn({}_0K_n) \quad . \quad . \quad . \quad \text{(ii.)}$$

So that the value of the coefficient of diffusion K_n at any definite concentration n is found from the above expression, involving the slope of the experimental curves shown in Fig. 2.

The values of the coefficient of diffusion in C.G.S. units thus obtained at the definite concentrations indicated in the first column are tabulated below, and these figures are plotted graphically in the accompanying curves (Fig. 3), which also include, for purposes of comparison, the results obtained by other workers in this subject.

Normality.	KCl. $K_n \times 10^5$	KNO_3. $K_n \times 10^5$	NaCl. $K_n \times 10^5$
0·05	1·388	1·453	1·165
0·10	1·430	1·421	1·170
0·20	1·467	1·374	1·177
0·40	1·493	1·319	1·188
0·60	1·504	1·276	1·198
0·80	1·515	1·233	1·208
1·00	1·527	1·190	1·216
1·50	1·555	...	1·235
2·00	1·584	...	1·253

§ 6. *The End-Correction.*

In order to test whether the correction to the length of the tubes in the apparatus β was small enough to be negligible, a third pair of diffusion flasks was made, in one of which were placed 15 parallel tubes, longer and thinner than hitherto employed, and in the other was sealed a single similar tube. These tubes were each roughly 5 cm. long and 0·08 sq. cm. in cross-section. The more exact dimensions of the various tubes are given below :—

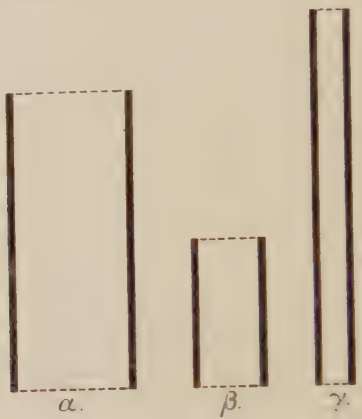
Apparatus γ.

Length.	Area.
4·954 cm.$=L_2$	0·0750 sq. cm.$=A_2$
4·952	0·0859
4·954	0·0816
4·950	0·0802
4·950	0·0873
4·953	0·0810
4·949	0·0878
4·951	0·0874
4·954	0·0766
4·952	0·0744
4·952	0·0827
4·954	0·0771
4·954	0·0875
4·952	0·0807
4·951	0·0849
4·952	0·0749
Mean length 4·952 cm.$=L_1$	1·2300 sq. cm. total area$=A_1$

With this apparatus the steady state is not reached until 10 days after commencing an experiment. The results obtained for the various solutions indicated are included in the following table :—

Apparatus.	20 per cent. KCl.		5 per cent. KCl.		2 per cent. NaCl.	
	$K\times10^5$	Expt. No.	$K\times10^5$	Expt. No.	$K\times10^5$	Expt. No.
α..........	1·526	28	1·486	7, 15	...	...
β..........	1·554	10, 11	1·473	6, 12, 14	1·170	51, 52
γ..........	1·550	43	1·462	44	1·184	54

The agreement exhibited in the results shown above, using the same solution in *different* apparatus, is as good as that obtained when the *same* apparatus is employed in different experiments, as will be seen by referring to the tables in § 4, and this is evidence that any end-corrections in the tubes used in this investigation are negligible. The relative dimensions of the diffusion tubes used in the three sets of apparatus are shown in the annexed diagram, and it will readily be granted that experiments made with such tubes should furnish a good test of the point under examination. Moreover, the concentration-gradient is reduced $2\frac{1}{2}$ times between β and γ, so that it is clear that the coefficient of diffusion is independent of the concentration-gradient.



§7. *Effect of Diffused Salt.*

It is desirable to demonstrate that the contamination of the bath of distilled water by the salt which diffuses from the flasks has no appreciable effect in retarding the rate of diffusion. This was tested in an experiment by replacing the distilled water by a weak solution (0·1 per cent.) of the salt employed.

Although so dilute, this solution is much stronger than would result from the diffusion in an ordinary experiment, and yet no greater difference was found in the result than is obtained when the experiments are conducted in the usual way, provided that, in all cases, the quantity introduced into the calculation of the coefficient of diffusion is the *difference* in the concentration of the solution at the two ends of the diffusion tube. The results are tabulated below :—

Expt. No.	Concentration.	Temp. in °C.	$K \times 10^5$.	Remarks.
10	20 p.c. KCl.	18·7	1·550	Pure water in bath.
11	,,	18·8	1·558	
27	,,	18·6	1·541	
26	20·1 p.c. KCl.	18·4	1·544	0·1 p.c. KCl in bath

§8. *Effect of Material of Tank.*

In order to test whether the material of which the tank is made affected in any way the rate of diffusion, the original tank which contained the bath of distilled water, made of tinned copper, was replaced by a large glass accumulator tank of about 30 litres capacity. The result of the experiment No. 27 is included in the previous table, and demonstrates that no effect greater than that due to experimental error is caused by the tank employed.

§ 9. *Discussion of Results.*

The general conclusions to be drawn from the results of the research are that (i.) in solutions of KNO_3 the diffusivity increases as the solution becomes more dilute; (ii.) in the case of KCl the opposite effect occurs; (iii.) with NaCl the value of the coefficient of diffusion decreases but slightly as the concentration becomes smaller.

In all, 54 experiments have been carried out in the investigation described in this Paper. The results of the first five have been omitted, as it was in these that the method was tested of filling the diffusion tube to half its height with the solution under examination, over which pure water was placed. It has already been mentioned that this method was discontinued on account of the inconsistencies found to be associated with it. Of the remaining 49 experiments in which this method of filling was not employed, all have yielded satisfactory results, and none has been omitted, with the exception of No. 13, in which a sudden and unusually large rise of temperature in the middle of July, 1912, caused such a disturbance that no steady state was reached.

Inspection of the graphs (Fig. 3) shows a considerable difference, not only in the absolute values of the diffusivity found by different observers, using different methods, but also in the general shape of the curves. As an example in the case of KCl, Oholm (" Zeit. für Phys. Chem.," 50, p. 309, 1904-5) obtains a curve indicating that the coefficient increases with the dilution, but Thovert (" Com. Rend.," 133, p. 1197, 1901 and 134, p. 594, 1902) obtains the opposite effect. Moreover, Oholm's results are generally lower than Thovert's. It becomes necessary to consider the probable accuracy in the various methods used by experimenters in diffusion. Oholm used what may be called a " burette method," in which various specimens of the solution were run off and analysed chemically. This is a modification of one of Graham's methods (" Phil. Trans.," 183, 1861) and is a favourite, having been used by Scheffer (" Ber. Deut. Chem. Gesell. " 16, 1903, 1883; " Zeit. für Phys. Chem.," 2, 390, 1888), by Euler (" Wied Ann."

63, 273, 1897) and by Von Hevesey ("Phil. Mag.," 25, 390 1913).

According to the author's experience, such a method cannot be expected to yield very accurate results. A disturbance much smaller than that involved in withdrawing the specimen layers of solution for analysis causes quite fatal consequences.

On the other hand, Thovert used an interference method of determining the distribution of concentration in the diffusion cell. Such a method may be quite free from mechanical disturbance, but small temperature changes and consequent convection currents would be liable to produce severe disturbance of the displacement of the interference fringes.

Thovert measured this displacement at different levels in the diffusion cell and at two different times, so that his method is not one in which the steady state is employed.

In the present method the disturbance is quite negligible; it is only during the few minutes necessary to complete a weighing that there is any disturbance at all, and even then the movement of the suspended system is limited to [illegible] mm. Moreover, the method possesses the advantage of employing the steady state. The results as indicated by the graphs are in distinct disagreement with those of Oholm, and follow the general shape of Thovert's conclusions. The agreement in the case of NaCl is very satisfactory, especially at the lower concentrations, but in the case of the other two salts my results are lower than those of Thovert, and I should be glad of the opinion of the Fellows as to the cause of this difference.

The research has been carried out in the laboratories of Birkbeck College, by the aid of a Government grant received through the Royal Society, and the author would like to record his indebtedness to Dr. Griffiths, head of the Physics Department at Birkbeck College, for his continued interest.

REFERENCES.

	Vol.	Page.	Year.
Schuhmeister, "Wien. Akad. Ber."	79(2)	603	1879
Scheffer, "Ber. Deut. Chem. Ges."	15	788	1882
Scheffer, "Ber. Deut. Chem. Ges."	16	1903	1883
Scheffer, "Zeit. für Phys. Chem."	2	390	1888
Euler, "Wied. Ann."	63	273	1897
Thovert, "Com. Rend."	133	1197	1901
Thovert, "Com. Rend."	134	594	1902
Oholm, "Zeit. für Phys. Chem."	50	309	1904-5
Clack, "Proc." Phys. Soc.	21	863	1908
Clack, "Phil. Mag."	16	—	1908
Clack, "Proc." Phys. Soc.	24	40	1911
Somers, "Proc." Phys. Soc.	25	74	1912
Von Hevesey, "Phil. Mag."	25	390	1913

ABSTRACT.

The Paper describes modifications made in the apparatus previously described (" Proc." Phys. Soc., XXIV., Dec. 15, 1911) to determine the value of the coefficient of diffusion of salts through water, by means of which the steady state is hastened and results obtained more quickly.

The single wide tube previously employed is replaced by a battery of shorter and narrower tubes. The error due to end-correction is investigated and results are given for the salts KCl, KNO_3 and NaCl for various concentrations down to very dilute solutions.

DISCUSSION

Dr. **Griffiths** said that he wished he could detect some flaw in Mr. Clack's methods, as he had always got higher results than those of the author. It appeared, however, to be much easier to get results too high than too low.

Mr. **Paterson** did not see why, in a symmetrical arrangement, such as the diffusion bulbs used by the author, the syphoning on which the maintenance of the concentration at the lower end of the diffusion tube depended should take place.

Mr. F. E. **Smith** wished to know if the author's method would be suitable for measuring the rate of diffusion of one solution into another of very nearly equal concentration and density. The problem was met with in standard cells. There was a slight difference in composition of the liquid throughout the cell, and this appeared to become practically constant after some years as though diffusion had ceased altogether.

Dr. **Russell** congratulated the author on having completed such a thorough investigation. When Glasgow University was removed to its new buildings at Gilmorehill in 1871, Lord Kelvin set up many long tubes containing liquids with the idea that the progress of the diffusion might be noted not only after years, but after hundreds of years. Although the author's earlier experiments had lasted months in some cases, he was now able to complete them in a few days.

The **Author**, in reply, thought it was an accident which way syphoning started, but when started it would obviously go on. It would be difficult to apply the method to solutions of nearly equal concentration, although it would measure the diffusivity of a strong solution with respect to a weaker one of the same salt to the same degree of accuracy as it measures that of a dilute solution with respect to water, the difference of concentration being the same in each case.

V.—*Note on the Conduction of Electricity at Point Contacts.*

By A. F. Hallimond, *Geological Survey and Museum, Jermyn Street.*

The experiments here described were undertaken with a view to clearing up, if possible, one or two questions which suggested themselves during the examination of a number of minerals for "unilateral conductivity."

The subject has already given rise to a considerable literature, but as this has recently been very fully summarised in the "Proceedings" of this Society* references will here be given only to such Papers as bear immediately on the points under discussion.

The present Paper relates purely to the conductivity of "point contacts" when a steady, or slowly varying, E.M.F. is applied, and no attempt will be made to deal with the effect of high-frequency oscillations.

According to the usual practice the results are presented as "characteristic," or volt-ampere curves for the respective contacts. To obtain these curves it has been usual to take readings on ampere- and volt-meters, and from them to plot the characteristic on squared paper. Since, however, for the present purpose a large number of curves were required, a form of mirror galvanometer was used by which the characteristic was directly plotted as the path of the spot of light on the screen. The arrangement was of the ordinary rocking mirror type, and need not therefore be described in detail. One coil (of low resistance) was connected as amperemeter, the other as voltmeter. Thus the co-ordinates of the deflection were those of the characteristic curve.

An arrangement of this type is naturally not capable of the same accuracy as dial instruments, but, on the other hand, the curves obtained can be followed continuously, and any sudden change in the conductivity of the crystal contact is immediately indicated by a violent displacement of the spot of light. The time taken to plot one curve is about 15 seconds.

The first part of this note consists of a description of the behaviour of a typical point contact (zincite and tellurium), in terms of which the results for the other pairs can be described.

---

* P. R. Coursey, "Proc." Lond Phys. Soc., Feb., 1914.

The second half of the paper deals with the results of a systematic examination of the forty-five contacts which are possible between the ten substances employed. The question to be answered may be put briefly thus: If the behaviour of the contacts between substances A and B and A and C is known, can any rule be found for predicting the behaviour of the third combination B and C? A partial solution of the problem has been attempted by the arrangement of the ten substances in a series.

1. *The Behaviour of a Typical Point Contact* (*Zincite-Tellurium*).

The use of natural cleavage surfaces is not advisable, as these are frequently coated with a film of altered material. A polished surface of zincite was therefore employed, the fragment being imbedded in fusible metal, and the tellurium was in the form of a polished globule fused on the end of a pin. The pin was inserted in a lever which pressed it down on the zincite surface, different weights being hung on the end of the lever. For other substances which required lighter contacts the lever was replaced by a very light spring. The weights are given in grams at the contact.

The diagram (Fig. 1) shows the types of curve obtained. Under light weights the contact tellurium-zincite was relatively a non-conductor for voltages up to about 5 volts. As the weight increased (100 to 500 grams) the current passing with zincite negative became appreciable, increasing more rapidly than that with zincite positive. Thus the well-known unilateral curve was obtained. This is marked AA′ in the figure, and will be referred to as type A throughout this note.

With still further increase in weight the conductivity improved, but experiments in this direction were terminated by the breaking either of the tellurium globule or of the zincite.

Contacts such as galena-tellurium (Fig. 3), which give the A curve under a weight of 1 gram or less, become good conductors under increased weight (10 grams) and their characteristic then resembles that marked BB′; it is not linear, but the asymmetry is greatly reduced. It seems fair to assume that the same effect would be observed with zincite if the material were strong enough to stand the weight required.

An effort was now made to find the limits to which the A curve could be pursued on raising the voltage. It was found that when a certain point was reached (from 1 to 6 volts according to the contact) the curve terminated in a sudden breakdown of resistance (AB, Fig. 1), and on lowering the voltage the tracing point returned along a much steeper curve, which passed through the origin at an angle corresponding with a resistance of 500 ohms or less, and could be pursued to some distance beyond it (BB′). The voltage at which this breakdown occurred was on an average higher with zincite positive than when it was negative. This curve is marked BB, and will be termed type B. It persists, at any rate for some hours, in most contacts, and it seems clearly due to a definite change of condition due to the breakdown.

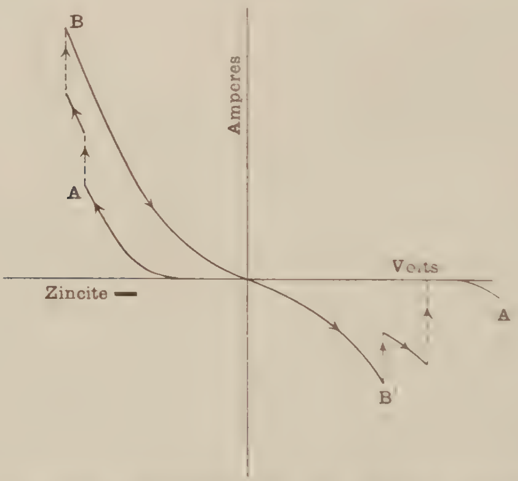


Fig. 1.—The Diagram Represents the Two Types of Curve Commonly Encountered.

The curve marked A A′ is the common unilateral curve. B B′ is the result of applying excessive voltage, and these are respectively termed types A and B throughout the Paper.

The dotted lines indicate the movement of the spot of light on breakdown and on recovery. The breakdown is sudden, the recovery is relatively slow.

This curve BB in its turn was now examined under increasing voltage. With zincite negative it underwent further alterations, becoming more and more linear in form, with decreasing resistance. If it had been caused by a breakdown of the A curve with zincite positive it generally remained permanent, but if the original breakdown had occurred with zincite negative, a very remarkable recovery could be obtained in the following manner.

If the voltage was raised to a certain point (generally from 1 to 4 volts) with zincite positive and the contact was then allowed to stand, the current could very frequently be seen to diminish more or less rapidly, so that the spot of light returned toward the A curve (point B′, Fig. 1). In favourable circumstances the A curve was actually regained and could then be repeated in its original form. If the recovery was partial the resulting curve was of an intermediate character throughout its course, as indicated by the short curves in the figure.

The following table of readings on an amperemeter will give some idea of the progress of such recoveries.

Contact Copper-zincite, standing after alteration with Zincite Positive.
(*E.M.F., approx.* 2.5 *volts.*)

Time.	Current.		
	Expt. *a*.	*b*.	*c*.
0	...	...	...
10	215	186	210
20	200	180	202
30	198	179	197
40	194	178	189
50	191	177	184
60	189	173	182
70	184	170	...
80	180	168	...
90	184	168	172
100	182	170	172
Seconds.	Micro-amperes.		

2. *Comparison of the Results given by Polished Contacts of Ten Substances taken in Pairs.*

Curves of the type described above were obtained in every case,* though not with the same facility, for in some cases the contacts required were extremely light.

The great similarity of the unilateral curves is well known to all who have had occasion to plot curves for various contacts, it is illustrated in the two curves reproduced in Figs. 2 and 3. Since the curves, especially the A type, are strongly unilateral in character, it is possible, for the purposes of classification, to describe the effect by giving the signs + and — respectively

---

* It will be observed that all these curves are convex toward the axis along which the voltage is measured. The theory recently discussed by Eccles ("Proc." Lond. Phys. Soc., June, 1913) requires for many cases curves which are concave. No such curves were observed in any of the contacts here described.

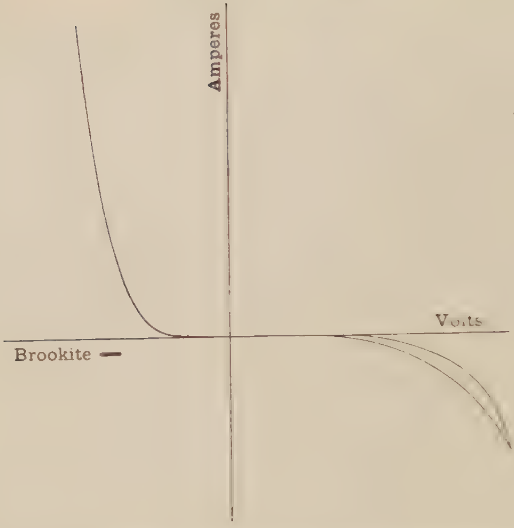


Fig. 2.—Curve of Type A for the Contact of Brookite with Galena.

The B type does not seem to be obtainable by pressure, as neither brookite nor zincite will withstand the increase of weight which might be expected to yield it. The weight for the curve shown is already 350 grams.

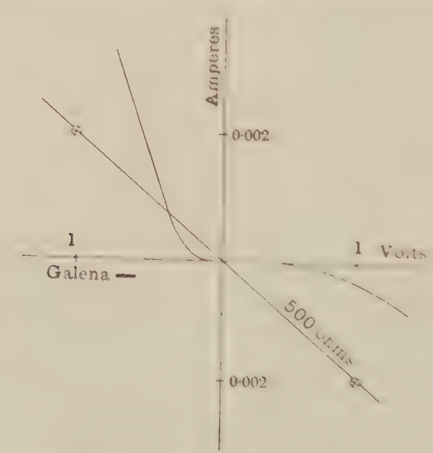


Fig. 3.—Curve of Type A for the Contact of Galena with Tellurium.

The similarity of this with Fig. 2 can leave little doubt that the same effect is being observed, although the weight is here of the order of 1 gram. The B type is readily obtained on increasing the weight, or by application of excessive voltage.

The straight line illustrates a direct method of ascertaining the scale; it is the "characteristic" of a 500-ohm voltmeter. The scale of the other figures is approximately that shown here.

None of these curves show irregularities greater than would be expected from the errors of tracing, except where definite breakdown has occurred.

to the two substances in contact; thus, quite arbitrarily, zincite might be called negative to tellurium, tellurium positive to zincite.

When this has been done a table can be prepared, such as that below, in which the sign given in each square describes the curves given by the corresponding mineral in the top line when in contact with the mineral named in the column on the left.

In this table, as first drawn, the distribution of the negative signs was at first sight quite arbitrary, but by changing the order of the minerals named it was found that all the negative signs could be brought below the diagonal as in the following table :—

—	Zincite.	Brookite.	Molybdenite.	Chromium.	Galena.	Iserite.	Chalcocite.	Copper.	Chalcopyrite.	Tellurium.
Zincite										
Brookite	—									
Molybdenite	—	—								
Chromium	—	*	—							
Galena	—	—	—	—						
Iserite	—	—	—	—	—					
Chalcocite	—	—	—	—	—	—				
Copper	—	—	—	—	—	—	—			
Chalcopyrite	—	—	—	—	—	—	—	—		
Tellurium	—	—	—	—	—	—	—	—	—	

From this it is at once evident that the 45 results can be expressed by means of a series of the ten substances, such that the higher member behaves toward the lower as zincite to tellurium.

It should be said that the substances used were selected as typical and uniform in composition. It is most probable that another set of even the same minerals, taken from other localities, would yield a somewhat different series. Further,

---

* Decisive results were not obtained for this contact.

the effect may be dependent on the orientation of the planes in contact. For these reasons no attempt has been made to give either the locality or the composition of the minerals used; they merely represent certain samples of material.

3. *Conclusions.*

Comparison of these results throws some light on the nature of the effect represented in the unilateral curves.

In the first place (to choose an example which is for the most part established by results published by previous observers) the characteristics given by all the substances here examined, when in contact with zincite under a weight of 1,000 grams, were almost identical in shape. It therefore seems fair to assume that the unilateral effect here obtained is a property of the zincite, and is independent of the physical constants of the other substance used.

The same reasoning may be applied to the contacts of, say, galena with substances standing below it in the table.

Now it is evident that the same substance (*e.g.*, galena) may play one of two distinct parts in a point contact. Toward substances higher in the series, such as zincite, it is in the position which has been called positive. Toward substances below it, such as tellurium, it is negative. What, then, is the condition which determines its behaviour? The answer to this question seems to lie in the fact that, as far as the very rough measurements go, the weight† required to obtain the unilateral curve diminishes progressively along the series, from about 1,000 grams for the zincite contacts to extremely light pressure for the contact of chalcopyrite with tellurium.

This being the case, it is evident that the substances below zincite, when under weights of 1,000 grams, will act alike as good conductors, the resistance of the contacts with zincite being only that of the zincite surface layer in every case.

---

† It will be noted that weights, not pressures, are here given. In these contacts the softer substance is spread over a certain area on the harder surface. Thus for a given weight the area increases as the substance is softer, but the pressure is correspondingly diminished. If the conductivity of the contact depends jointly on the area and pressure, it will then be roughly independent of the hardness of the substances in contact. The fact that the curves were alike for contacts of zincite with chromium and zincite with molybdenite under 1,000 grams, the area of the latter being about 1 square millimetre, renders it clear that some such assumption is necessary, though the statement that the conductivity is directly proportional to the pressure can only be taken as a rough approximation to the true relationship.

Under lighter weight galena, say, in its turn possesses a high surface resistance which yields a unilateral curve in contact with tellurium.

Many experiments will suggest themselves by which these conclusions could be tested, but it is impossible to discuss them within the limits of this note, of which the chief aim is to present a plea for the examination of the effect on strictly experimental lines. The serial arrangement suggested is advanced as a tentative solution to the question put forward on p. 76. Whether it survives further examination or not it may perhaps serve as a basis for the discussion of the large number of " rectifying " contacts now known.

ABSTRACT.

The Paper deals with the " characteristic " or volt-ampere curves given by various " Point " contacts when the voltage is slowly varied. The curves were plotted by means of a form of rocking mirror galvanometer, which projected the characteristic as the path of a spot of light on the screen, the co-ordinates being respectively proportional to the current and voltage.

The first part describes the behaviour of a typical contact, zincite-tellurium. The well-known unilateral curve is terminated by a sudden breakdown of resistance, after which the contact has a more symmetrical characteristic of lower resistance at the origin. By allowing the contact to stand under a certain voltage with zincite positive it may frequently be restored to the condition of high resistance in which it again yields the unilateral curve.

The second part describes the results obtained on examining the characteristics for the forty-five contacts possible between 10 chosen substances. The conclusion is reached that the results in all cases are similar to those given by zincite-tellurium. No line could be drawn separating " metallic " contacts from those in which one or both conductors were " crystals."

The results obtained are expressed in terms of a series in which the higher member behaves towards the lower as zincite to tellurium.

Series : Zincite, brookite, molybdenite, chromium, galena, inserite, chalcocite, copper, chalcopyrite, tellurium.

In the third part the conclusion is drawn that in a contact yielding the unilateral (high resistance) curve, the resistance lies within the surface of the member standing higher in the series. Rough measurements showed that the weight required in these contacts diminished from about 1,000 grams for zincite to very light contact for the substances lying near tellurium, and it is suggested that this gradation in weight determines the relative positions arrived at for the respective substances.

DISCUSSION.

Mr. Duddell thought the author's method of obtaining continuous curves much more satisfactory than the ordinary method, as it gave less chance of the point contacts altering during the experiment, and, further, the arrangement of the minerals in the table he gave appeared to have some correspondence with their order of sensibility when used as wireless detectors.

Mr. D. Owen attributed much of the success of the author's experiments to the attention paid to the preparation of polished surfaces of contact. It would be useful if the author would specify the curvatures employed. The two types of characteristic might be accounted for by the greater or less extent to which the electrostatic attraction between the contacts extend, type B occurring when that effect was large. Calculation proved that, assuming a P.D. of only one volt, and a distance apart of 10^{-7} cm. (ten times the molecular distance), the electrostatic pull was of the order of 1,000 gm. *wt. mm*$^{-2}$. It might in some cases be much greater than this.

Mr. P. R. Coursey thought the main point of interest in the Paper was the table in which the substances were arranged in the order of the effects obtained with them. It would be of considerable use if some connection could be found between the arrangement of the substances in this table and some of their chemical or physical properties, as it should then be possible to extend the present limits of the table to include new substances, and in this way, it may be, to obtain perhaps even more sensitive wireless detectors than were at present available.

The visual method of taking the characteristic was of value for rapid investigation of the behaviour of any particular contact, and in this connection he would ask the author whether in his experiments employing this method he obtained any evidence of a "hysteresis" effect in the contact. A number of experimenters had stated that such an effect does exist, and it should be an easy matter with this arrangement definitely to decide the point for any contact or specimen.

With reference to the jumping of the characteristic from the "A" to the "B" type of curve by the application of excessive voltage, it seemed evident that this must be what happened when a strong "X" was received by a detector; but it does not, however, seem to explain an effect that he had noticed (and others had obtained similar results) when using a zincite-tellurium contact as a detector, that the impact of a strong atmospheric very often does not spoil the reception of signals, but sometimes they are actually stronger after it has passed. This may occur several times in succession, each time the strength of the signals rising somewhat, till finally a steady state seems to set in, in which signals are much louder than it was possible to obtain at first.

The author mentions in the Paper that on no occasion has he obtained characteristic curves *concave* to the volt axis, although Dr. Eccles's theory indicates that such should be possible. On one occasion he had obtained a curve of a particular zincite bornite contact that was concave to the volt axis on the side with zincite positive, but was convex with the zincite negative, while, moreover, it seemed to be a stable condition as the curve could be repeated (slide shown). It appears, however, to be rather a peculiarity of the specimens employed than a property of the materials, as with other samples he had failed to obtain any such result. It seemed probable, too, that if the voltage limits had been taken higher the curve might have turned and become convex to the volt axis for the higher values.

Prof. Fortescue communicated the following: The curves given in Fig. 1 are very interesting. I have repeatedly noticed the same thing with the zincite and galena series of contacts. The breakdown is apparently due to increase of area of the contact, brought about by the increase of mechanical pressure or by the softening, or even fusing, of one of the materials when high voltages are applied. The restoring effect of the reverse current is not so easy to explain; possibly it may be some electrolytic action. I have never found a point which had been rendered conductive by heavy mechanical pressure restored in this way. The tabulation of the substances given on page 2 can also be carried out from their thermo-electric properties with similar results. Carborundum, however, presents a difficulty, as it can be strongly positive or negative, and is to a large extent independent of the mechanical pressure.

The AUTHOR, in reply, said that it seemed likely that some correspondence would exist between the order of the substances in the table and the behaviour of the contacts as detectors. If the conclusion of Pierce is accepted, that the characteristic is still followed under high frequencies, the point of best sensitiveness for weak signals should lie near the maximum curvature. The discussion of this question is scarcely possible within the limits of the present note. The ease of adjustment is an important factor in practice; it seems dependent on two conditions: (1) The breakdown may supervene before the bend in the A curve is reached. This is especially true of the metals. (2) The weight permissible for a given contact pair lies between a lower value, for which both surfaces are poor conductors, and an upper limit at which they conduct yielding a relatively symmetrical curve. The further apart the bodies are in the series the greater is the range of weight over which they give the A curve, and the greater, therefore, is the ease of adjustment.

He had not so far been able to connect this series with one derived from other physical properties. Hysteresis, such as was described by Pierce, was observed. This, however, he would assign to alteration and recovery. If the breakdown in Fig. 1 is made less marked, the curve becomes extremely similar to the hysteresis curve. In some experiments the change was so slight that even with the mirror the step was not obviously discontinuous. The action of an X on the detector can scarcely be predicted from the change in the characteristic alone. It would be interesting to see the nature of the characteristics immediately before and after such an alteration. If the X was strongly damped the first impulse might tend either to breakdown or to recovery. The curve shown by Mr. Coursey was extremely interesting. He had traced several curves for zincite-bornite, but had not encountered this form.

The curvature of the surfaces appeared to be immaterial. The form of the area of contact would apparently be that of a small element of the harder surface. Provided the radius of curvature were not comparable with the diameter of contact, the area would be virtually plane; for this reason no special shape beyond that of a blunt point was attempted. Different considerations might, of course, apply to the use of splintered points of mineral. The electrostatic attraction does not seem to offer of itself any possibility of a unilateral effect, since the force on interchanging + and — signs would be the same. Some unilateral property would still be required. In the case of zincite the area in most cases was nearer 0·01 sq. mm. than 1·0. This would require a higher potential gradient, of the order 10^9 volts per centimetre. As the dielectric strength of mica is only 2×10^6 volts per centimetre, the strain in the intervening space would be considerable. If the electrostatic pull were the direct cause of conductivity in the B curve, the curves A and B should be tangential at the origin, for here the pull has a negligible effect on the natural resistance of the contact. As far as could be seen, the two curves cut at a finite angle. Possibly the mechanical breakdown of some film might be assumed, but the high weights in zincite contacts offered difficulties.

The recovery of the contact was undoubtedly one of the most difficult features of these curves. It seemed impossible to conceive a mechanical change which would be reversible to such an extent. The writer felt that the published thermo-electric data which he had encountered were too few and conflicting to permit a comparison with any degree of certainty. The behaviour of such a mineral as pyrite, which exists in two widely different thermo-electric forms, should yield interesting information.

The very high weights required by carborundum would suggest that it should behave in the same way as zincite, possibly lying beyond it in the table. A very good unilateral curve was published by Pierce,* and this curve has the high current with carborundum negative, "current (in the crystal) toward the platinised surface," as would be expected. The difficulty with carborundum may arise in some cases from the incomplete contact with the fusible metal, and also from the possibility that many of the curves under light pressures were very probably of the B type. Like cassiterite,† carborundum‡ appeared to be a colourless substance, owing its colour and possibly its conductivity to dissolved matter. The variations in the electrical properties of such bodies were probably very great.

---

* G. W. Pierce, THE ELECTRICIAN, December, 1907, p. 375.

† Th. Liebisch, "Sitzungsber. d. K. Preuss. Akad. d. Wiss," 1911, 414.

‡ "Zeit fur Kryst," L., 33.

VI. *Thermal Conductivity. Part II.: Thermal Conductivity of Badly-conducting Solids. By* THOMAS BARRATT, *A.R.C.S., B.Sc.*

RECEIVED OCTOBER 13, 1914.

I. Introduction and Historical.

A NEW method of measuring the thermal conductivity of solids was recently described by the author,* and the method was applied to the determination of the conductivity of certain of the rarer metals and alloys at air temperatures and at 100°C.

The same arrangement—with one or two modifications—has now been employed in the measurement of this property in the case of badly-conducting solids. The results are given in detail in the following Paper. A number of typical substances have been tested—*e.g.*, woods, both hard and soft; common electrical insulators, such as glass, fused silica, ebonite, and firebrick; and in addition, carbon, which is a partial conductor of electricity. The results indicate that the method adopted is as successful in the case of these substances as it proved to be when pure metals and alloys were under investigation. Perhaps the most interesting point in connection with these measurements is the fact that precisely the same method, and in the main the same apparatus, have been employed both for metals and non-metals. Up to the present time the methods adopted for the determination of the thermal conductivity of non-metallic substances have been essentially different from those used in the case of metals, so that the present series of experiments affords an opportunity for the first time of a direct comparison of the conductivities of the two classes of solids.

The experiments of Lees,† of Jäger and Diesselhorst,‡ and of the present author § have shown that the thermal conductivities of some of the pure metals—notably bismuth and lead—are of the same order of magnitude as those of some of the non-metals. For example, quartz and graphite gave results considerably higher than those of bismuth (Lees, and Barratt, *loc. cit.*). In the following investigation the results obtained for bismuth and lead by Jäger and Diesselhorst have been adopted as a starting point, and the conductivities of the non-metals deduced by direct comparison.

---

* T. Barratt, "Proc." Phys. Soc., XXVI., Part V., pp. 346-371, Aug., 1914.

† C. H. Lees, Bakerian Lecture, Roy. Soc., 1908.

‡ W. Jäger and H. Diesselhorst, "Abh. d. Phys. Tech. Reich.," 3, 269, 1900.

§ T. Barratt, *loc. cit.*

Of the methods employed up to the present time, the disc arrangement of Lees and Chorlton,* and of Lees,† is perhaps the most accurate and best known. This method has been used, with unimportant modifications, by several experimenters, including A. Eucken,‡ some of whose results are alluded to in a later section of the present Paper. (*See* Section 5.)

Another arrangement, similar in some respects to that of Lees, was adopted by Biquard, for the measurement of the thermal conductivity of heat insulators. The material was in the form of a circular plate, surrounded by a guard-ring of copper, thus securing a normal flow of heat, this being supplied by a current of warm water maintained at a constant temperature. On the plate and guard-ring were placed concentric boxes full of broken ice. The rate of melting of the ice gave an indication of the heat supplied. The method is in some respects similar to that employed by Berget for the conductivity of metals, and shares with it the disadvantage that the temperature of the side of the plate next the warm water is not the same as that of the water. Again, the presence of the metallic thermometers employed interferes considerably with the uniformity of the flow of heat through the specimen, and with its temperature as given by these thermometers. In the method described in the present Paper the specimen is completely bare from end to end, the platinum thermometers employed being in positions quite removed from the solid itself.

A totally different arrangement was that employed by Clement and Egy § in the measurement of the thermal conductivity of fireclay. The substance was in the form of a cylinder, 40 cm. long, 12 cm. diameter, and was heated electrically by a nickel wire spiral passing through a hole along its axis. The temperatures at various distances from the axis were measured by thermo-couples, whose presence must lead to the same distortion of the flow of heat as noted above in Biquart's method.

---

* Lees and Chorlton, "Phil. Mag.," [5], 41, 495, 1896.

† C. H. Lees, "Phil. Trans.," 191, 399, 1898.

‡ A. Eucken, "Ann. d. Physik.," 34, pp. 185-221, February 3, 1911.

§ J. K. Clement and W. L. Egy, "Met. and Chem. Eng.," 8, pp. 414-416, July, 1910.

A somewhat similar method, again, was employed by R. Melmer,* in the case of substances such as fats, earth, and sands. A thin central platinum tube, within which was a mercury thermometer, was heated by an electric current. Concentric with this was a wider tube of brass, the substance being tightly packed in between the two tubes. Measurements were made of the heat supplied and of the temperatures of the platinum and the brass, and the thermal conductivity deduced.

2. *Arrangement of Apparatus.*

The substances tested were in the form of accurately turned cylinders of diameter 5 mm. or 6 mm., and of lengths from 5 cm. to 20 cm. Each cylinder was lightly and uniformly painted over with a dead-black varnish, consisting of an aniline dye dissolved in amyl acetate. One end of the cylinder AC (Fig. 1) fitted accurately into a slightly conical hole bored in a copper cylinder CC, of length 4 cm., inner diameter 6·5 mm. Around CC was wound 3 metres of single silk-covered pure platinum wire, gauge 30. Around this coil of wire a single layer of shellac varnished silk paper was pasted. Over this again was another copper cylinder, C′C′, whose thickness increased from zero at one end to about 2 mm. at the end into which the cylinder AC fitted.

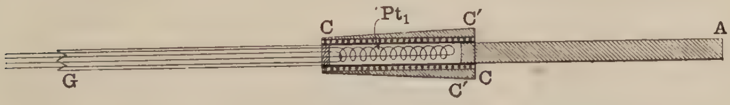


FIG. 1.

Inside the inner cylinder was a platinum thermometer Pt_1, which gave the temperature of the end C of the cylinder AC. A thin glass tube CG served to keep the apparatus steady and in the centre of a water or steam jacket which enclosed the whole apparatus, and maintained its temperature constant. This temperature was registered by a second platinum thermometer, Pt_2, which rested within the outer jacket just opposite the middle point of the specimen AC. The difference of temperature (V) between the "hot" end of the cylinder AC and the enclosure was thus given by the difference of the readings (Pt_1-Pt_2) of the two platinum thermometers. The ends of the platinum wire wound round the inner cylinder were connected to a carefully calibrated potentiometer, which, in connection with a standard one-ohm coil, enabled one to obtain the current (C) through the wire, and the E.M.F. (E) at its ends. The arrangement of the potentiometer, &c., was precisely the same as that described in the Paper already referred to on the "Thermal and Electrical Conductivities of some of the Rarer Metals and Alloys." (T. Barratt, *loc. cit.*)

---

* R. Melmer, "Akad. Wiss. Wien.," Sitz. Ber. 120, pp. 269-281, March, 1911.

It was shown by the author in this Paper that the thermal conductivity "k" of a substance under the above conditions is given by

$$k=\frac{\mathrm{H}^2\coth^2 al}{pqh\mathrm{V}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where H is the heat received by the cylinder at its hot end,

p is its perimeter,

q its cross-sectional area,

h the heat lost from 1 sq. cm. of its surface per second per 1° C. difference from its surroundings,

V the difference of temperature between the hot end of the cylinder and the enclosure,

l the length, and

$$a=\sqrt{\frac{hp}{qk}}.$$

When l is long enough, this expression reduces to the very simple form

$$k=\frac{\mathrm{H}^2}{pqh\mathrm{V}^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

and the latter form of the equation has been employed in nearly every case treated in the present series of experiments.

A simple proof of this latter equation, from first principles, may be of interest.

Let the cylinder be placed in a gas at zero temperature.

The amount of heat per second through a plane at distance x from the hot end (which is at temperature V) is

$$-kq\frac{dv}{dx}.$$

The heat through a parallel plane at distance $x+dx$ is

$$-kq\frac{dv}{dx}+\frac{d}{dx}\left(-kq\frac{dv}{dx}\right)dx.$$

Hence the heat lost from the surface (of area $p\,.\,dx$) between these planes is

$$kq\frac{d^2v}{dx^2}dx=pdxhv.$$

Multiply each side of this equation by $2\frac{dv}{dx}$ and integrate.

$$\therefore \qquad kq\left(\frac{dv}{dx}\right)^2=hpv^2+\mathrm{A}.$$

If the length of the cylinder is such that a part of it is at the temperature of the enclosure, we have, at points where $v=0$,

$$\frac{dv}{dx}=0.$$

Hence $$\mathrm{A}=0,$$

and $$kq\left(\frac{dv}{dx}\right)^2=hpv^2. \qquad \text{(A)}$$

This equation is applicable at every point of the cylinder. At the hot end, where $v=\mathrm{V}$,

$$\mathrm{H}=-kq\frac{dv}{dx}. \qquad \text{(B)}$$

Hence, from (A) and (B),

$$qk\frac{\mathrm{H}^2}{q^2k^2}=hp\mathrm{V}^2,$$

or $$k=\frac{\mathrm{H}^2}{pqh\mathrm{V}^2}.$$

The amount of heat (H) given to the specimen cylinder is equal to $\frac{\mathrm{CE}-\mathrm{C'E'}}{\mathrm{J}}$, where C, E, are the current and E.M.F. respectively with the specimen in place; and C′E′ are corresponding quantities when the specimen is replaced by a copper plug whose end is flush with the end of the copper cylinder, CC, the excess of temperature, V, being maintained the same in both cases. A correction, which is in some cases a comparatively large one, has to be made for the heat lost from the exposed end of the copper plug. This is done by adding to "H" as calculated above a quantity (H′) obtained by the product of q, h and V. The accuracy attainable in this correction is, however, just as great as that obtained in the main experiment.

In performing an experiment, the specimen is put into position, the current turned on, and the apparatus left for one or two hours till conditions have become steady, when C, E, and V are carefully measured. The cylinder is then removed, the copper plug substituted, and the current adjusted so as to keep V the same as before. (This latter operation takes only a few minutes, so that little or no alteration of temperature takes place within the enclosure.) C′ and E′ are then quickly determined. The arrangement of the electrical part of the apparatus is the same in all respects as that employed by the author in the case of metals, in the Paper referred to above, and it is therefore unnecessary to describe it in detail.

3. *Determination of "h."*

In order to determine the amount of heat, "h," lost per second by 1 sq. cm. of surface of the substance when its temperature is 1°C. above that of its surroundings, it is clear that in consequence of the very low electrical conductivity of the specimens employed, a direct method is inconvenient, if not impossible.

From equation (1), however, we obtain

$$h = \frac{H^2 \coth^2 al}{pqkV^2}.$$

Assuming Jäger and Diesselhorst's results for the thermal conductivity of bismuth or lead, the remaining quantities on the right-hand side of this equation can be obtained by the same series of measurements as are made in the main experiments. This has therefore been done in the case of pure lead and of pure bismuth at temperatures 20°C. and 100°C., and the mean results of a great number of experiments gave the values of "h" as follows:—

"h" at 20°C. $=0·000224$; "h" at 100°C. $=0·000265$.

Below are recorded the measurements made in two of these experiments.

BISMUTH.

July 7th, 1914. Temperature 20°C.
Radius, $r=0{\cdot}300$ cm., $pq=2\pi^2r^3=0{\cdot}533$; $k=0{\cdot}0194$.
$V=Pt_1-Pt_2=9{\cdot}190$°C., $H'=qhV=0{\cdot}00058$.

1. With bismuth rod in place.	2. With copper plug in place.
$Pt_1-Pt_2=9{\cdot}190$°C.	Pt_1-Pt maintained 9·190°C.
*E=6283	$E'=5122$
*C=388·7	$C'=317{\cdot}2$
†W=3898	W=3898

* C and E are readings on potentiometer, in ohms, corresponding to current through wire, and E.M.F. at its ends, respectively.

† W is the reading when a Weston cell is in place.

The true " E " is obtained from the expression E/W × E.M.F. of Weston cell, and similarly for true current " C."

Hence $H=(CE-C'E')/J=0{\cdot}01334$.

$H'=qhV=0{\cdot}00058$.

True " H "$=0{\cdot}01392$, and $H^2=0{\cdot}0001938$.

" h " at 20°C.$=(H^2\coth^2 l)/(pqkV^2)=0{\cdot}000223$

LEAD.

July 11th, 1914. Temperature 100°C.
Radius $r=0{\cdot}267$ cm., $pq=0{\cdot}3756$; $k=0{\cdot}082$.
$V=7{\cdot}044$°C.; $H'=qhV=0{\cdot}00047$.

1. With lead in place.	2. With copper plug in place.
$Pt_1-Pt_2=7{\cdot}044$°C.	Pt_1-Pt_2 maintained 7·044°C.
E=7153	$E'=5263$
C=365·8	$C'=269{\cdot}2$
W=3897	W=3897

Hence $H=0{\cdot}01963$; $H'=0{\cdot}00047$.

True $H=0{\cdot}02010$; $H^2=0{\cdot}0004040$.

and " h " at 100°C.$=(H^2\coth^2 al)/(pqhV^2)=0{\cdot}000265$.

The values obtained for " h " at 100°C. in the case of bismuth showed good agreement with those for lead; and, similarly, for both metals at 20°C. This affords a verification of the values for the thermal conductivity of these metals as given by Jäger and Diesselhorst in the Paper already referred to. The rods of bismuth and lead employed in the experiments detailed above were of sufficient length to make the value of $\coth^2 al$ almost negligible in each case.

4. *Determination of Thermal Conductivity, "k."*

In order to determine the thermal conductivity, k, the procedure already detailed in sections 2 and 3 was followed. In the calculation of "k" from these measurements the values of "h" previously obtained, viz. 0·000224 at 20°C. and 0·000265 at 100°C., were substituted in the equation, $k=(\mathrm{H}^2 \coth^2 al)/(pqh\mathrm{V}^2)$, and the thermal conductivity, k, at once deduced.

Below are given full details of two of the experiments, together with the method of reducing the results.

RED FIBRE.
July 15th, 1914. Temperature 20°C.
Radius $r=0·336$ cm. ; $pqh=2\pi^2r^3h=0·0001677$

1. Specimen in place.	2. Specimen replaced by copper plug.
$\mathrm{P}t_1-\mathrm{P}t_2=\mathrm{V}=10·191$°C.	V maintained at 10·191°C.
E=5687	E′=5360
C=3495	C′=329·5
W=3900	W=3900

E.M.F. of Cadmium Cell=1·0186 volt.

$$\text{True current}=\mathrm{C}/\mathrm{W}\times 1·0186.$$

$$\text{True E.M.F.}=\mathrm{E}/\mathrm{W}\times 1·0186.$$

$$\text{Heat given (H)}=(\mathrm{EC}-\mathrm{E}'\mathrm{C}')/\mathrm{JW}^2\times(1·0186)^2+qh\mathrm{V}.$$

$$=0·003609 \text{ calories.}$$

Hence "k" at 20°C. $=(\mathrm{H}^2 \coth^2 al)/(pqh\mathrm{V}^2)=0·00112$.

RED FIBRE.
Sept. 8th, 1914. Temperature 100°C.
Radius $r=0·336$ cm., $pqh=0·0001984$.

1. Specimen in place.	2. Specimen replaced by copper plug.
$\mathrm{P}t-\mathrm{P}t_1=\mathrm{V}=10·57$°C.	V maintained at 10·57°C
E=7060	E′=6693
C=359·7	C′=340·1
W=3879	W=3879

Heat given $=(\mathrm{EC}-\mathrm{E}'\mathrm{C}')/(\mathrm{JW}^2)\times(1·0186)^2$; $qh\mathrm{V}=0·005143$ calories.

k at 100°C. $=(\mathrm{H}^2 \coth^2 al)/(pqh\mathrm{V}^2)=0·00119$.

In the accompanying table (Table I.) are given the experimental details relating to the measurement of the thermal conductivity of all the metals tested, both at air temperatures and at 100°C.

TABLE I.—*Thermal Conductivity of Non-metals at 20°C. and 100°C.*

Substance.	Date.	Temp. °C.	Radius (r) (cms.)	$qh \times 10^7$	$pqh \times 10^7$	E (ohms)	C (ohms)	E′ (ohms)	C′ (chms)	W (ohms)	H(cals) $\times 10^6$	V (Cent.)	Length (cms.)	Density gms. p. cc.	$k \times 10^4$
Fused Silica	July 27	20°	0·332	775	1,618	5,886	369·2	5,433	340·4	3,890	6,037	9·75	6·1	2·17	23·7
	Aug. 26	100°		917	1,914	7,140	363·2	6,584	334·7	3,879	7,385	10·57			25·5
Soda Glass	July 27	20°	0·332	775	1,618	5,699	357·2	5,340	331·5	3,890	5,095	9·64	6·0	2·59	17·2
	Aug. 26	100°		917	1,914	7,044	358·3	6,584	334·7	3,879	6,242	10·57			18·2
Red Fibre	July 15	20°	0·336	794	1,677	5,687	349·5	5,360	329·5	3,900	4,420	10·19	5·9	1·29	11·2
	Sept. 8	100°		1,039	1,984	7,060	358·7	6,693	340·1	3,876	5,413	10·57			11·9
Fire-Brick	Sept. 12	20°	0·336	794	1,677	5,924	369·5	5,614	350·0	3,874	4,541	10·57	5·5	1·73	11·0
	Sept. 2	100°		1,039	1,984	6,985	354·8	6,651	337·9	3,879	4,900	10·57			10·9
Ebonite ...	Sept. 12	20°	0·327	752	1,546	5,703	355·1	5,635	351·4	3,874	1,535	10·57	6·3	1·19	1·36
	Sept. 2	100°		889	1,829	6,728	341·9	6,653	338·0	3,879	1,789	10·57			1·31
Gas Carbon	July 25	20°	0·251	443	699	5,932	370·2	5,337	332·9	3,892	7,279	9·51	14·1	1·42	85·0
	Aug. 27	100°		524	827	7,329	372·5	6,574	334·0	3,880	9,354	10·57			95·0
Mahogany	Sept. 14	20°	0·325	743	1,517	5,633	350·6	5,459	339·5	3,874	2,936	10·57	5·5	0·55	5·09
	Aug. 25	100°		879	1,795	6,876	349·2	6,630	336·9	3,880	3,760	11·42			6·05
Satin Walnut (along grain)	July 28	20°	0·325	743	1,517	5,692	352·9	5,536	342·4	3,891	2,603	10·10	5·9	0·50	4·36
	Aug. 29	100°		879	1,795	6,798	345·1	6,586	334·4	3,879	3,296	10·57			5·42
Satin Walnut (across grain)	July 29	20°	0·332	775	1·618	5,474	341·4	5,398	336·6	3,892	1,633	10·13	4·8	0·50	1·60
	Aug. 29	100°		917	1,914	6,706	340·5	6,586	334·4	3,879	2,304	10·57			2·48
Oak	July 27	20°	0·325	743	1,517	5,521	345·5	5,336	332·8	3,892	3,029	9·61	6·3	0·65	5·83
	Aug. 31	100°		879	1,795	6,843	347·5	6,617	335·9	3,857	3,485	10·57			6·07
Lignum vitæ......	July 21	20°	0·334	785	1,647	5,693	349·6	5,476	336·5	3,898	3,206	10·16	6·8	1·16	6·04
	Sept. 1	100°		928	1,949	6,881	349·2	6,617	335·9	3,879	3,948	10·57			7·16
Greenheart	July 21	20°	0·334	785	1,647	5,847	364·4	5,534	344·6	3,894	4,468	10·39	7·5	1·08	11·2
	Sept. 1	100°		928	1,949	6,958	353·5	6,617	335·9	3,879	4,888	10·57			11·0
American whitewood	July 13	20°	0·325	743	1,517	6,384	387·1	6,210	377·2	3,901	3,105	12·49	6·5	0·575	4·07
	Sept. 3	100°		879	1,795	6,838	346·7	6,648	337·7	3,880	2,998	10·57			4·48
Boxwood	July 28	20°	0·327	752	1,546	5,742	356·0	5,592	346·6	3,891	2,408	10·28	5·7	0·901	3·56
	Sept. 10	100°		889	1,829	6,858	348·5	6,684	339·7	3,879	2,927	10·57			4·14

The results have all been corrected in the following particulars :—

1. Calibration of coils of resistance boxes used in potentiometer.

2. Standardisation of the one-ohm resistance coil and of the three cadmium cells used.

3. Calibration of coils of platinum resistance bridge, and reduction of platinum temperatures to the hydrogen scale.

The instruments used were precisely the same as those employed in the determination of the thermal conductivity of pure metals and alloys in the Paper mentioned before.

The correction due to the "resistance at the joint" between the specimen and the copper block into which it fitted is eliminated in the present series of experiments, being allowed for in the determination of "*h*." when a bismuth or lead cylinder is employed. It may be assumed that the "joint resistance" is the same in the case of the bismuth or lead as when the other (similar) cylinders are substituted in their place under precisely the same conditions.

5. *Discussion of Results.*

The values obtained in the present Paper for the thermal conductivities of non-metals agree in most cases very well with those recently obtained—that is, where corresponding results are available. In Table II. a comparison is made of these quantities.

TABLE II.

Substance.	Thermal conductivity. (Present Paper).	Thermal conductivity. (Previous results).
Soda glass.........	0·00172 at 20°C. 0·00182 at 100°C.	0·0013 to 0·0018 (K and L) 0·00227 (12° to 32°) (P).
Ebonite............	0·000136 at 20°C 0·000131 at 100°C.	0·00042 (L). 0·00038 at 90°C. 0·000089 (F).
Gas Carbon.......	0·0085 at 20°C. 0·0095 at 100°C.	0·0012 (K and L).
Mahogany.........	0·000509 at 20°C.	0·0005 (L).
Oak	0·000605 at 100°C. 0·000583 at 20°C. 0·000607 at 100°C.	0·0006 (K and L).
Firebrick..........	0·00110 at 20°C. 0·00109 at 100°C.	0·0024 (H. L and D)

K and L refers to Kaye and Laby's Tables, pub. Longmans, Green & Co., 1911.

L: C. H. Lees, *loc. cit.*

P: O. Paalhorn, Diss. Jena, 1894.

D: A. Dina, Rend. Inst. Lombardo, 32,205, 1899.

F: Forbes, "Proc." Edinb. Soc., 8, 62, 1874-75.

H L and D: Herschel, Lebour and Dunn, Rep. Brit. Soc., 49, 1879.

It is to be expected that values obtained for similar substances should differ rather widely, as it is obviously impossible to obtain specimens identically alike of any particular substance of the classes dealt with here. Even in the investigation of thermal conductivities of the metals most observers have noted the marked influence of even a minute percentage of impurity. This influence is, of course, much more powerful in the cases under investigation in the present research.

It appears from the results that most non-metallic substances conduct heat more readily at higher temperatures. The same result has been noted by several other observers, notably Clement and Egy,* in the case of various samples of fireclay; and Eucken† in investigations on the conductivity of amorphous bodies. The latter observed (as in the experiments of the present author) that the thermal conductivity of ebonite did not change much with the temperature. The same observation may be made of the conductivity of "red fibre" and of firebrick.

The results of the present series of experiments seem to indicate that the conductivity of most kinds of wood increases very rapidly indeed with the temperature. Too much significance, however, must not be attached to this, as continual heating at 100°C. probably has the effect of altering very considerably the structure of the wood. Experiment showed that constant results at 100°C. could not be obtained until the wood had been kept at this temperature for several hours. All the materials tested were therefore treated in this way before the final measurements were made.

A slight modification of the arrangement described above is being employed in an attempt to determine the thermal conductivity of liquids.

The research has been carried out at the Wandsworth Technical Institute, and my thanks are due to the Principal and Governors of that Institute for their kindly interest in the experimental work.

ABSTRACT.

The thermal conductivities of a selection of non-metals at 20°C. and 100°C. have been determined by precisely the same method, and in the main the same apparatus as was recently employed by the author in the determination of the "Thermal conductivity of some of the rarer

---

* J. K. Clement and W. L. Egy, *loc. cit.*

† A. Eucken, *loc. cit.*

metals and alloys." The substances treated were in the form of accurately turned cylinders, placed in an enclosure at constant temperature. Measurements were made of the heat given (electrically) to one end of the cylinder, and of the temperatures of this end and of the enclosure, and the thermal conductivity deduced from a simple formula. A table of results is given, which agree well with those obtained by Lees and other observers in cases where a direct comparison is available.

DISCUSSION.

Dr. **Haker** mentioned that the formula used by the author assumed that the isothermal surfaces in the specimen were plane. This would not be far wrong in the case of good conductors, but it might introduce serious error in the case of substances such as those now treated. He also doubted the validity of the assumption that "h" was proportional to V for any but very small differences of temperature. The results given in the Paper for firebrick were about 20 times lower than those given by other observers, including recent determinations of his own

Mr. F. E. **Smith** asked why the author put his second thermometer inside the enclosure maintained at a constant temperature. If the enclosing vessel is of metal, and water at constant temperature circulates, is it not better to take the temperature of the water? There must be a temperature gradient between the hot rod and the enclosing vessel. The second P*t* thermometer lies on the gradient. Does the author assume the P*t* thermometer to have the same temperature as the enclosing vessel? With regard to the temperature distribution at the hot end of the rod, he was at first of opinion that the author was in error, but afterwards found it difficult to make a definite statement owing to lack of data. He would, however, be glad if the author would give the solution of the following problem. Instead of a poor conducting rod, imagine a rod of an absolute insulator with regard to heat (*i.e.*, it is impossible to change its temperature) to be used. Then no heat can be given to the P*t* thermometer from the end of this rod, and it appears that the temperature of the heater must be higher than before if the P*t* thermometer has the same temperature. Will the author give his ideas as to the distribution of temperature in this case and that when the copper plug is substituted, in order to see whether it is likely that the conductivity of the rod would come out zero? He did not like the symbols used by the author, and thought it would have been simpler to give the energy rather than readings of E.M.F. and resistance.

Dr. **Russell** said that it was important to know how much of the heat was lost by radiation and how much by convection currents. The author's emissivity constant seemed to include both. With ordinary copper wires suspended in air it was known that about 90 per cent. of the total heat emitted was taken away by convection currents, and only about 10 per cent. was lost by radiation. Newton showed that the convected heat carried away was proportional to the difference of temperature between the cooling body and the surrounding medium, and hence, so far as the convection loss was concerned, the author's assumption was justified. Stefan's law applied to the radiation loss, and, strictly speaking, the assumption that this loss was proportional to the difference of temperature was only permissible for small differences of temperature. Luckily, however, this loss was small, and he did not think that the accuracy of the results obtained was appreciably affected by the assumption.

The **Author** communicated the following reply: The points raised by Dr. Harker are, I believe, in each case due either to misapprehension or to misprints in the advance proofs. In the first place, the diameters of the specimens were 5 to 6 *millimetres* (not centimetres, as given in *one* part of the Paper). The ratio of the sectional area to the thermal conductivity thus remains approximately the same as in the experiments on metals. This part of the criticism applies to practically all recent determinations of the thermal conductivity of metals where the dimensions of specimens are of the same order as in the present experiments. As Dr. Russell remarks, Newton's law of cooling is applicable to that part of the heat lost by convection, and also very nearly to that lost by radiation, provided the excess of temperature of the rod is not great. In the present research this excess of temperature was no greater than 10·6°C. Finally, the value of "k" in the case of firebrick is that given in the main table of results—viz., 0·0010. The value referred to by Dr. Harker is again a misprint. In reply to Mr. Smith, it is unsafe to put a bare platinum thermometer in water or steam, and, in addition, the temperature to be measured (Pt_2) is that of the enclosure, which may be (especially at steam temperatures) slightly different from that of the "jacket." I feel certain there is little or no temperature gradient within the enclosing vessel, as the water equivalent of the latter is enormously greater than that of the rod, which is, in addition, never more than 10°C. higher than that of the enclosure. With regard to the problem proposed by Mr. Smith, there is no such thing as a perfect heat insulator. It may be safely assumed that the "hot" end of the rod acquires the temperature of the copper cylinder as given by the thermometer Pt_2. It might happen, however, that the rods were of such low conductivity that a smaller amount of heat is lost from it than from the end of the copper plug ($h.q.V$). This contingency is allowed for in the calculations, for the value of $CE - C'E'$ would then become negative. In the extreme case given by Mr. Smith, $CE - C'E'$ would be just equal to $h.q.V$, and would, therefore, give a zero value for H, and therefore also for the conductivity.

VII. *Ionisation.* *By* Sir J. J. Thomson, *O.M., F.R.S.*

By ionisation we mean the production in a medium, whether solid, liquid or gaseous, of particles charged with electricity which can be set in motion by an electric field and produce a current of electricity through the medium. Ionisation can be brought upon in many ways: By light, as when light falls on a metal surface, or when ultra-violet light of less than a certain wave-length passes through a gas: by Röntgen rays, which ionise solids and liquids, as well as gases, when they pass through them; by cathode rays, by positive rays, by heat as in the gases in a flame, by solution, by bubbling gases through liquids. In some cases possibly by chemical action, though in the great majority of cases the ionisation is due to the heat produced rather than to any special ionising effect due to chemical change. We know, for example, many cases of chemical action which are not accompanied by ionisation. The combination of hydrogen and chlorine is a conspicuous one, another is the dissociation of nickel carbonyl, which takes place at comparatively low temperatures, but is not accompanied by ionisation.

What is the nature of the carriers of these electric charges?

We must distinguish here between two different questions: (*a*) The nature of the carriers when they are first produced, and (*b*) when they have got into equilibrium with their surroundings. The study of the mobility of the ions, the speed at which they diffuse through the surrounding gas, or their velocity when acted on by given electric forces has thrown considerable light on the second question, the nature of the ions when in equilibrium. The most important properties brought to light by researches on the mobility of the ions are the following:—

1. The mobility of an ion depends only on the nature of the gas through which it is moving, and not upon the gas from which the ions are produced. Thus, if we ionise by Röntgen rays a mixture of iodine vapour and hydrogen gas, some of the ions will arise from the ionisation of the iodine and others from that of the hydrogen, the mobilities of the two kinds of iron through the mixture are the same.

2. Through a considerable range of pressures, the mobilities are inversely proportional to the pressure. In the case of the negative ions when the pressure is reduced below that due to a centimetre or so of mercury the mobility increases much

faster with diminution of pressure than this law indicates. Some recent experiments by Mr. Todd indicate that a similar result is true for positive ions, though the pressure at which the abnormality sets in is very much lower than for negative ions.

3. When the density of a gas remains constant the mobility of ions through it is independent of the temperature through a wide range of temperature.

4. The mobilities through several gases, such as hydrogen, argon, nitrogen, are very approximately inversely proportional to the square roots of their atomic weights; this is not true for easily condensed gases, and there are some exceptions to it for the more permanent ones.

5. The mobility does not depend on the charge on the ion—*i.e.*, it is the same for singly as for doubly charged ions.

Theories of the Mobility of Ions.

Expressions for the mobility of ions through gases have been worked out on two assumptions: (1) That the effects of collisions between ions and molecules are similar to those between two hard elastic spheres, and (2) that the effects produced by the molecules on the ions are the results of attractive forces between the atoms and molecules varying inversely as the fifth power of the distance between them; this law represents the force between a charged particle and an uncharged conductor when the distance between the two is large compared with the linear dimensions of the conductor. On the first theory I find, taking into account "persistence of velocities" (*see* Jean's "Dynamical Theory of Gases," p. 236), that R, the velocity of the ion under unit electric force, is given by the equation,

$$R=\frac{e}{N\pi\sigma^2\sqrt{M}\,.\,\Omega}\left\{\frac{M_1+M_2}{M_1M_2}\right\}^{\frac{1}{2}}\frac{5}{4}\left(\frac{M_2+3M_1}{M_2+5M_1}\right),$$

or

$$R=\frac{e}{N\pi\sigma^2\sqrt{M}\Omega}\left(\frac{M_1+M_2}{M_1M_2}\right)^{\frac{1}{2}}\frac{5M_2'+(M_1+3M_2)}{15M_2^2+10M_1M_2-M_1^2},$$

according as M_1 is greater or less than M_2. N is the number of molecules of the gas per unit volume, M the mass of a hydrogen molecule, Ω its average velocity at the temperature of the gas, M_1 the mass of an ion, M_2 that of a molecule, σ the sum of the radii of an ion and a molecule, and e the charge on an ion.

Let us first consider the variation of R with the masses of either the ion or molecule.

If $$M_1 = M_2,$$

$$R = \frac{e}{N\pi\sigma^2\sqrt{M}\,.\,\Omega}\frac{5}{6}\sqrt{\frac{2}{M_2}}.$$

If M_1 is large compared with M_2, then

$$R = \frac{e}{N\pi\sigma^2\sqrt{M}\,\Omega}\frac{3}{4}\sqrt{\frac{1}{M_2}}.$$

Thus, if σ were unaltered, the mobility of an ion would become independent of its mass as soon as that became a considerable multiple of that of the molecule of the gas through which the ion was moving. The fact that the mobility of all ions through the same gas is the same implies on this theory that all the ions should be of the same size, and, what is still more remarkable, since in many gases the mobility of the ions varies inversely as the square root of the atomic weight, it follows from the expression for R that for all these gases σ should have the same value—*i.e.*, that in all these different gases the ions should be of the same size. From the values of the coefficients of mobility for positive ions I have calculated the relative values of σ for the positive ions in a number of gases: the results are given in the following table:—

Gas	σ^2
H_2	62·0
O_2	63·8
He	61·5
Cl_2	56·5
N_2O	69·0
CO_2	69·0
CO	90·0

These values are on an arbitrary scale: the absolute value of σ calculated by the same formula for hydrogen is $\frac{2}{\pi} \times 10^{-7}$cm. the value usually assigned to the diameter of a molecule of hydrogen is $2 \cdot 1 \times 10^{-8}$cm. Thus the diameter of the cluster formed by the ion and a hydrogen molecule is about π times the diameter of a hydrogen molecule. Thus, though the ion is bigger than the molecule, it is not extravagantly so, and as the size of the ions in different gases tend to equality, the disproportion between the sizes of the ions and molecules would be less for the heavier and larger molecules than for those of hydrogen. In the case of easily condensed gases, such as ammonia gas, the vapours of alcohol and ether the size of the ions is considerably greater than for the more permanent gases.

According to the expression for R given above, the effect of temperature on the mobility of the ion would depend upon the variation of $1/N\sigma^2\Omega$ with the temperature, or, when the gas is kept at constant volume, so that N is constant, of $1/\sigma^2\Omega$. But Ω varies as $\theta^{\frac{1}{2}}$ when θ is the absolute temperature, so that the temperature variation would be that of $1/\sigma^2\theta^{\frac{1}{2}}$. Now Phillips' experiments show that, through a considerable range of temperature, R for constant volume is independent of the temperature. This necessitates $\sigma^2\theta^{\frac{1}{2}}$ being constant. We may, perhaps, account for this in some such way as the following: The aggregates which form the ions are doubtless brought about by the condensation of the molecules under the attraction exerted by the electric charge at the nucleus of the ion. Statistical equilibrium will occur when the destructive effect of the collisions of the molecules against the aggregates is balanced by the condensation due to the electrical attraction, and the thermodynamics of this process shows that when this equilibrium occurs the work required to detach an uncharged molecule from the aggregate must be commensurate with the kinetic energy of a molecule of the gas—*i.e.*, must be proportional to the absolute temperature. If the uncharged molecule is regarded as analogous to a conducting sphere, and the electrical action of an ion as that due to a charge, e, at its centre, the work required to separate the uncharged molecule from the ion would be proportion to $\frac{e^2}{\sigma^4} \cdot v$, when v is the volume of the uncharged molecule. In equilibrium this is proportional to θ; hence $\frac{e^2}{\sigma^4}$ is proportion to θ or σ^2 proportional to $e\theta^{-\frac{1}{2}}$. Thus $\theta^{\frac{1}{2}}\sigma^2$ would be constant, and therefore R for constant density independent of the temperature.

As on this view $\frac{e^2}{\sigma^4}v$ is proportional to the absolute temperature, e/σ^2, and therefore R, should vary as $v^{-\frac{1}{2}}$, and thus the velocity of the ions through different gases should vary as $\frac{1}{\sqrt{M_2 v}}$, and not as $\frac{1}{\sqrt{M_2}}$, which is what the experiments indicate.

If we suppose that from time to time the positive ion attracts a corpuscle and remains connected with it for a short interval, the connection being so loose that it can be broken up by collision with the molecules without the aid of any external agent, such as Röntgen rays; the mobility as determined by many of the methods would be reduced by an amount depending on the proportion between the time the ion was free from the corpuscle to the time when it was in combination with it. This correction would depend on the intensity of ionisation, and would be greater when the ionisation was strong than when it was weak, and thus the mobility of the ions would depend upon the intensity of ionisation. No such effect has yet been discovered in gases at ordinary temperatures, and we conclude, therefore, that in these cases the correction is not important. On the theory indicated above, $\frac{e}{\sigma^2}$ depends only upon the temperature; thus σ^2 will be proportional to e, so that the mobility of the ion will not depend upon its charge. This is in agreement with experiment.

When the mass of the ion is very small compared with that of the molecules of the gas, as is the case when the negative ion is a corpuscle, the expression for R becomes

$$R = \frac{e}{N\pi\sigma_1^2\sqrt{M\Omega}}\frac{1}{\sqrt{M_1}}.$$

where σ_1 is now the radius of a molecule of the gas. Thus the mobility on this view is increased in the proportion of $\sqrt{M_2/M_1}$ in consequence of the diminution of mass; also in the proportion of σ^2/σ_1^2 in consequence of the corpuscle being so much smaller than the ion. In gases such as air, hydrogen, oxygen the velocity of the negative ion is a little greater than that of the positive at pressures down to a centimetre or so of mercury. At lower pressures it becomes much greater than that of the positive ion, and the ratio of the mobility of the negative to the positive increases as the pressure diminishes. This suggests that at these lower pressures the negative ion is for a considerable fraction of its existence a free corpuscle, but at times gets attached to a molecule or aggregate of molecules of the gas, when it moves much more slowly. After a time it can get detached from this aggregate by causes other than the primary ionising agent. The negative ion thus alternates between a free corpuscle and a negatively charged aggregate, and the mobility will depend on the relative times it spends in these conditions.

In the cases of argon and nitrogen very carefully freed from all traces of oxygen or water vapour, Franck and Pohl have shown that even at atmospheric pressure the mobility of the negative ion is as much as 200 times that of the positive one, showing that the negative corpuscles cannot attach themselves to molecules or aggregates of molecules of these gases. They have shown, too, that the presence of even a fraction of 1 per cent. of oxygen is sufficient to reduce the mobility of the negative ion to a value but little greater than that of the positive one.

Let us now consider for a moment another theory of the mobility of the ions, the theory which supposes that the motion of the ions through a gas is determined, not by collisions like those between elastic spheres, but by forces between the ions and the molecules varying inversely as the fifth power of the distance between them. Maxwell worked out the theory of diffusion for gases when the molecules repelled each other with forces varying inversely as the fifth power of the distance between them. We can easily adapt this theory to the case of an ion moving through molecules which it attracts with forces varying inversely as the fifth power of the distance. If we do this we find that R, the mobility, is expressed by the equation,

$$R=\frac{e}{NA}\sqrt{\frac{M_1+M_2}{M_1M_2K}},$$

where A is a constant, K the magnitude of the force between an ion and a molecule at unit distance, and, as before, e is the charge on an ion, M_1 and M_2 the masses of an ion and molecule respectively, and N the number of molecules per unit volume. It will be seen from this equation that as soon as M_1 becomes considerable with respect to M_2 the value of R depends but little on that of M_1. On this theory, then, if the ion is a cluster of molecules, the mobility will depend but little upon the number of molecules in the cluster, it does not in this case matter about the size of the cluster, as there is no factor corresponding to the σ^2 in the expression for R on the previous theory. Again, if K the measure of the force between an ion and a molecule, is independent of the temperature, R will, for a gas at constant volume, be independent of the temperature, a result indicated by Phillips' experiments. Again, if the force between the ion and the uncharged molecule is due to the charge on the ion, K will be proportional to e^2, so that R will be independent of the charge which is again in agreement with the facts.

We have seen that the mobility of the ions through several gases varies as $M_2^{-\frac{1}{2}}$; interpreted in the light of the preceding expression, this means that K is the same for all these gases.

This is a difficulty in the way of this theory. We should expect K to be proportional to the moment of the electrical doublet induced in the molecule by the charge on the ion when placed at unit distance from the molecule, but μ^2-1, if μ is the refractive index of the gas, is proportional to the moment of the electrical doublet induced in a molecule of the gas by a constant and uniform field of electric force: we should, therefore, expect K to be proportional to μ^2-1, and R to $\{(\mu^2-1)M_2\}^{-\frac{1}{2}}$, and not to $M_2^{-\frac{1}{2}}$. There is no doubt, however, that in many gases R is much more nearly proportional to $M_2^{-\frac{1}{2}}$ than to $\{(\mu^2-1)M_2\}^{-\frac{1}{2}}$.

Let us now consider what on this theory would be the mobility of a negative corpuscle: in this case M_1 is very small compared with M_2, so that the formula becomes

$$R=\frac{e}{NA}\sqrt{\frac{1}{M_1K}},$$

while the mobility of an ion through the same gas is

$$\frac{e}{NA}\sqrt{\frac{1}{M_2K}},$$

if the force between the ion and the molecule were like that between a point charge of electricity and a conducting sphere, or a sphere whose specific induction capacity was greater than that of the surrounding space, K would be the same for the ion and the corpuscle, so that the mobility of the corpuscle would be $\sqrt{M_2/M_1}$ times that of the ion; in the case of nitrogen, when $M_2/M_1=28\times1{,}780$, the mobility of the corpuscle would be about 220 times that of the ion, so that at 760 mm. pressure and 15°C. the mobility of the corpuscle would be about 200 (cm. sec.) (volt cm.). This is of the order found by Franck and Pohl for the mobility of the negative carriers in nitrogen carefully freed from oxygen. On the other theory of mobility, the mobility of a corpuscle would be more than four times this: for the mobility of the corpuscle is $\frac{\sigma^2}{\sigma_1^2}\sqrt{\frac{M_2}{M_1}}$, where σ is the sum of the radii of an ion and a molecule, and σ_1 the radius of a molecule, and σ is more than double σ_1.

Again, in those gases like hydrogen, helium, oxygen, nitrogen and argon, where R is proportional to $M_2^{-\frac{1}{2}}$, K must be constant, so that in all these gases the mobility of the corpuscle must be the same, a result which, as far as I know, has not yet been tested.

For gases such as the vapours of alcohol, water or ether, which have abnormally large specific inductive capacities in comparison with their refractive indices, I have given reasons for thinking ("Phil. Mag.," May, 1914) that some of the atoms in the molecule are positively, others negatively charged, so that the forces between these molecules and a charge of electricity would tend to vary rather as the inverse cube than the inverse fifth power of the distance. To these, therefore, the preceding theory would not apply, and as a matter of fact, the mobilities in these vapours are considerably less than those in the permanent gases.

The Communication of Electricity from a Gas to a Metal.

The study of the constitution and properties of ions leads to results which have an important bearing on the question of the communication of a charge of electricity from gas to a metallic electrode immersed in it. We have seen that in the inert gases, such as nitrogen and argon, the corpuscles in the gas do not attach themselves to the molecules. When they come into collision with these molecules they rebound in their original condition; the impact of a corpuscle against a neutral molecule or atom does not result in the charging of the atom. Again, to deprive a positively electrified ion of its charge a corpuscle must attach itself to the ion. This corpuscle must come from somewhere, and to detach a corpuscle requires the expenditure of a finite amount of energy. The study of positive rays again shows that to deprive some negatively electrified atoms of their charge, those of oxygen, hydrogen or carbon, for example, requires the expenditure of a considerable amount of work. We thus see many examples where the mere contact between the electrified body and a neutral one does not result in the transference of the electrification.

Let us apply these considerations to the case of a metal electrode immersed in an ionised gas. From what we have seen, it is unlike that the mere hitting of the ions against the metal will result in the transference of the charge from the gas to the metal; to effect this transference, in many cases at least, will require the expenditure of a finite amount of work. Where is this work to come from? The most obvious source of work of this kind is to suppose that if the metal is acting as an anode, negative ions or corpuscles accumulate in its neighbourhood, forming, with the surface of the anode, two layers of electrification, with a finite difference of potential between them. If V were this difference of potential then there would be an amount of work, V*e*, available to transfer a charge, *e*, from the gas to the metal. If *we* were the work required, for example, to transfer the negative charge on a negatively electrified oxygen ion, the transference of the charge from oxygen gas to the anode would not occur unless there was a difference of potential at least equal to *w* between the anode and the gas. Thus, we should expect to find considerable difference of potential between metal electrodes and the surrounding gas. This consideration is one that should be borne in mind in interpreting the results of some experiments on the discharge through gases. For example, it is often assumed that the potential in the interstices of a piece of wire gauze is the same as that to which the gauze is raised by its metallic connection with a voltaic battery. If double layers are formed round the wire of the gauze there may be a considerable difference of potential between the wires and the open spaces, so that the establishment of a retarding potential V between the wires of two gauzed screens may not be sufficient to stop all the rays with energy corresponding to V from passing through the screens. An example, which is interesting historically, of this effect is afforded by earlier investigations on the cathode rays. It was at first thought that these could not be charged particles, because they were not deflected by an electrostatic field, even when the charged plates used to deflect the rays were placed inside the vacuum tube. This want of deflection was due to the fall of potential between the plate being used up in the formation of double layers at their surface, so that the greater part of the space between the plates was comparatively free from electric force. When the pressure in the vacuum tube is very much reduced, the effect of these double layers is diminished, though even at the lower pressures which are now used for these experiments it is necessary to be alive to the fact that double layers may still be present, and that the electric force to which the cathode particles are exposed is not necessarily equal to the potential difference between the plates, divided by the distance by which they are separated. We should expect these double layers to be especially conspicuous in strongly electro-negative gases like oxygen and chlorine, which require a large amount of work to deprive them of their negative charge.

A conspicuous instance of the formation of a double layer is that at the anode in a vacuum tube through which a current of electricity is passing. This produces a change of potential close to the anode amounting in many cases to more than 20 volts, and it occurs so abruptly that it has hitherto been impossible to reach a point so close to the anode that the difference of potential between the anode and the point is less than this value. The experiments of Skinner show that it varies somewhat with the metal of the electrode, though the variations are not large and it does not vary much with the current density at the cathode. It is exceptionally large in chlorine. It may be regarded as the mechanism by which the necessary work is supplied (1) to get the negative charge from the ions in the neighbourhood, and (2) in some cases to liberate positive ions from the anode.

Experiments on the mobility, however, in the main give us information as to the size of the ion when it is in equilibrium with its surroundings; they give us but little information as to what is the nature of the ions when they are first formed, and therefore give but little information as to the processes by which ionisation is effected. It is, however, the mechanism of this process to which I wish to direct your attention rather than to its final product. Many of the points in this process are obscure and the investigation of them difficult and complicated; but the question is one of such importance that I think no apology is needed for bringing it before you this evening.

One point in the mechanism of ionisation seems quite clear—that is, that in, at any rate, the vast majority of cases of ionisation of gases, one part of the process of ionisation is the liberation of a corpuscle or electron. We know this, because, at very low pressures, and in the case of inert gases like argon even at high pressures, the measurement of the mobility and diffusion of the negative ions shows that these are many hundred times greater than the corresponding quantities for the positive ions. At higher pressures, on the other hand, the difference, except in the case of the inert gases, is comparatively small, for here the surrounding molecules have had time to condense round the electron and load it up before it is finally driven out of the gas. Thus, the process of ionisation involves the liberation of a corpuscle from the molecule, and is not primarily the splitting up of a diatomic molecule into two oppositely charged atoms.

One part of the process of ionisation is thus the ejection of a corpuscle from the molecule of the gas which is ionised. The violence with which the corpuscle is ejected depends to a great extent on the way the ionisation is produced, and the study of the way the velocity of the corpuscle on its departure from the atom varies with the type of the ionising agent gives some very interesting results. When a gas is ionised by Röntgen rays the corpuscles are expelled from the molecules with very high velocities; in fact, the experiments made on this subject point to the conclusion that the velocity with which the corpuscles are expelled does not differ greatly, if at all, from that of the cathode rays, which by their impact against the anti-cathode generated the Röntgen rays which ionised the gas. The existence of the high-speed corpuscles coming out of molecules exposed to Röntgen rays is clearly shown by C. T. R. Wilson's photographs of the distribution of the ions produced when a gas is exposed to Röntgen rays. We see that the drops of water which mark the situation of the ions lie along a series of detached fine curves, which mark the track of the high-speed corpuscles emitted when the gas is exposed to the rays. These high-speed corpuscles ionise the gas as they pass through it, each one of them producing a large number of ions; thus the greater part—in fact, practically the whole—of the ionisation in gases under Röntgen rays is produced, not directly by the rays, but indirectly by the rapidly-moving corpuscles which they eject.

The velocity of these fast corpuscles does not depend upon the nature of the gas, nor on the intensity of the rays, but only upon the quality—the hardness of the rays. The harder the rays the greater the speed of the corpuscles. A similar result holds when ultra-violet light is used instead of Röntgen rays. The velocity of the negative particles expelled from a metal plate under the influence of ultra-violet light does not depend upon the intensity of the light, but merely upon its wave-length. The experiments made by Mr. Hughes point to the conclusion that the velocity with which they leave the molecule, as distinguished from the velocity with which they leave the plate, does not depend on the kind of molecule, but merely on the wave-length of the light.

Thus the velocity of the particles expelled by means of radiation, whether this be light or Röntgen radiation, depends solely upon the quality of the radiation, and when this radiation has, as is the case with monochromatic light or characteristic Röntgen radiation, a definite frequency, the energy with which the corpuscles are expelled from the molecule is proportional to the frequency of the radiation. This is a result which might be expected from the "quantum" theory. The experimental results hitherto obtained seem on the whole to confirm this result, though it must, I think, be confessed that the direct experimental evidence in favour of the strict proportionality is too meagre to enable us to maintain that it is a direct result of experiment. There are many points on which we have no direct experimental evidence; for example, the energy measured is the maximum energy of the ejected particles; we do not know whether the energy of a corpuscle ejected from a molecule by monochromatic light has a constant value or whether it can assume a considerable range of values stopping at a definite maximum. The discrepancy between different experimenters on this subject is considerable, and it is not impossible that the limit they obtain for the maximum energy may depend on the sensitiveness of the recording instruments and the excellence of the insulation. In spite of this, it is abundantly proved, however, that the speed of the emitted corpuscles varies very rapidly with the nature of the ionising agent.

The energy acquired by the ejected particles under the influence of radiation is so great that it is very difficult to reconcile it with the idea that the energy in the radiation is uniformly distributed through space. On the assumption that the energy is uniformly distributed, we can calculate the maximum electric force in a beam of light of known intensity, and we find, after giving the greatest possible value to any resonance effect, that to account for the velocity of the ejected particles we should require uninterrupted trains of waves millions of wave-lengths long. This difficulty is overcome if we adopt a modification of an idea that I put forward some time ago. At that time it was thought that the total number of ions produced when a given beam of Röntgen rays was absorbed in a gas was the same for all gases, and I suggested that the Röntgen beam was made up of units, and that whenever an ion was liberated one of these units was absorbed. Subsequent experiments, however, showed that the number of ions produced by the absorption of a given beam depended to an appreciable extent upon the nature of the gas and also that the production of the ions was in the main due to the high-speed corpuscles ejected by the rays, and not to the rays themselves. Recent experiments by Barkla and Philpotts have shown, however, that, though the number of ions produced varies with the gas which absorbs the radiation, the number of the high-speed particles ejected is invariable, so that we may assign to these high-speed particles the rôle which I previously assigned to the ions, and suppose that the liberation of a high-speed particle from any gas whatever involves the destruction of one unit of radiation. We may picture to ourselves the process as being somewhat of the following type : We suppose that radiation, whether ordinary light or Röntgen radiation, is made up of units, and that these units are closed tubes of electric force, each tube possessing a definite amount of energy depending upon the type of radiation. Suppose, now, that one of these closed tubes, C, travelling through space passes near to a molecule of a gas, and that in this molecule there is a tube of force passing between a corpuscle, A, and the equivalent positive charge B. If, now, the part of C which passes nearest to AB is in the opposite direction to AB, the two tubes will attract each other, C getting pulled down to AB and AB up to C, as in Fig. 1 (A). If this process goes on until the tubes come into contact, as in Fig. 1 (B), fissure will take place as in Fig. 1 (C), and the two tubes C and AB will be replaced by a long tube with its ends anchored at A and B. Thus the closed

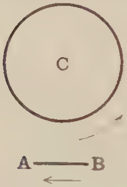


FIG. 1.

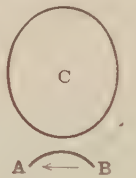


FIG. 1A.

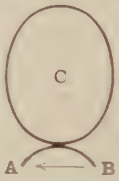


FIG. 1B.

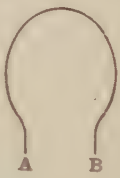


FIG. 1C.

free tube which could travel freely through space and formed a unit of the radiation, has ceased to exist, and has been replaced by an anchored tube ; thus one unit of radiation has ceased to exist. The anchored tube is in a state of tension, and therefore pulling at the corpuscle. This pull first detaches the corpuscle from the molecule, and then increases its velocity, so that the energy which was in the tube gets communicated to the corpuscle, and all but the work required to detach the corpuscle from the molecule appears as kinetic energy in the corpuscle. If the work required to detach the corpuscle is but a fraction of the kinetic energy it acquires, that kinetic energy will be approximately equal to the energy originally in the ring C, the unit of radiation, and so will practically be independent of the substance from which the corpuscle is liberated.

Let us now turn to another ionising agent—rapidly moving electrified particles. Let us first take the case of negatively electrified particles, cathode rays. We find that these cannot ionise a gas unless they possess more than a certain amount of energy. This amount can conveniently be expressed in terms of the voltage through which the atomic charge must fall to acquire the requisite amount of energy. This voltage, according to Franck and Hertz, is as follows :—

Hg	N	O	H	Ar	Ne	He
4·9	7·5	9	11	12	16	20·5 volts.

There is no apparent connection between these quantities and the chemical properties of the atom, nor, what is perhaps still more striking, with their power of acquiring a negative charge as contrasted with that of losing it. For example, neither the atoms of nitrogen and helium, the elements at the ends of these series, acquire negative charges in the positive rays, while those of oxygen and hydrogen readily do so ; again, argon and neon, which are also in intermediate positions, do not.

When cathode rays with more than the ionising energy move through these gases they expel corpuscles from some of the molecules against which they strike. The numerous experiments which have been made on the velocity of corpuscles expelled in this way have led to some extremely interesting results.

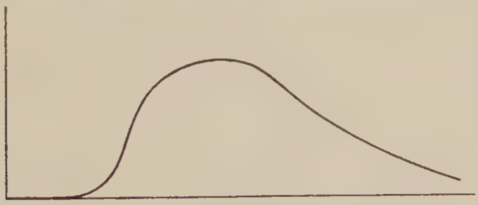


FIG. 2.

It has been found that the velocity of these corpuscles is practically independent of the velocity of the cathode rays which drive them out of the molecules, and that the maximum energy is not above that acquired by the fall of the atomic charge through about 10 volts ; thus, even though the cathode particles have speeds corresponding to that represented by thousands of volts, the corpuscles they eject, or, at any rate, the great majority of them, move little if at all faster than those liberated by rays which have a speed represented by 20 or 30 volts. The number of the corpuscles liberated by a cathode particle when moving through 1 cm. of gas at a definite pressure is represented by a curve of the type shown in Fig. 2. The ionisation does not begin until the cathode rays have a certain amount of energy. It then increases rapidly, attains a maximun which, in the cases investigated by Kossel, was when the cathode rays had energy corresponding to about 300 volts, then diminishes slowly at first, but ultimately inversely as the energy of the cathode particle. A curve almost identical with this has been shown by Gehrts ("Ann. der Phys., XXXVI., p. 1003) to represent the secondary cathodic radiation excited when a plate of metal is bombarded by cathode rays of different speeds. Here, as in the case of gases, the speed of the secondary rays does not seem to depend much upon that of the primary. The most obvious explanation of ionisation by cathode rays is that a corpuscle in the atom acquires from a cathode particle moving past it sufficient energy to enable it to escape from the atom. The energy Q communicated to a particle at rest of mass M by a moving particle of mass m, starting with the velocity V, is given by the equation,

$$Q=\frac{\frac{4mM}{(M+m)^2}T}{1+\frac{d^2 \cdot 4}{e^2E^2}T^2\left(\frac{M}{m+M}\right)^2},$$

where T is the kinetic energy of the cathode particle, e, E the charges on the particle and corpuscle respectively, and d the perpendicular from the corpuscle on the initial path of the particle. If the corpuscle requires an amount of energy, W, to free it from the atom, the particle will only eject the corpuscle when

$$d^2<\left\{\frac{4mM}{(M+m)^2}\frac{T}{W}-1\right\}\frac{e^2E^2}{4T^2\left(\frac{M}{m+M}\right)^2}.$$

The number of ions per centimetre of path of the cathode particle will be proportional to the limiting value of d^2, and thus, regarded as a function of T, will vary as

$$\frac{1}{T^2}\left\{\frac{4mM}{(M+m)^2}\frac{T}{W}-1\right\}.$$

Thus ionisation will not begin until

$$T=\frac{(M+m)^2}{4mM}W,$$

and will be a maximum when T has twice this value ; for large values of T the ionisation will be inversely proportional to T. When we compare this with the results found by experiment we see that, though some of the more striking phenomena are accounted for by the theory, there are others which are not in accordance with the theory in this form. One of these is the fact that the energy of the primary cathode rays when the ionisation is a maximum is much greater than twice the energy when ionisation first begins. This, however, could be accounted for by supposing that of the corpuscles in the atom some require more energy than others to eject them from the atom. There may be one group that requires W_1 units of energy to escape, another W_2 and so on; thus ionisation will begin when the primary cathode rays have energy equal to W_1, and though the detachment of this group will be a maximum when the energy of the cathode rays is $2W_1$, yet, as the energy of the cathode rays increases, the other groups of corpuscles may begin to be ejected, with the result that the energy of maximum ionisation is raised. If there are n_1 corpuscles which require energy W_1 to eject them, n_2 requiring W_2, we are putting $M=m$ in the equation that the ionisation will be a maximum when

$$T=\frac{2\Sigma n}{\Sigma\frac{n}{W}},$$

and will begin when $T=W_1$; in this case the energy for maximum ionisation cannot be calculated from that for initial ionisation. To avoid subsidiary maxima, of which the curves connecting the ionisation with T show no indication, W_2 must be $<2W_1$ and $W_3< 2(n_1+n_2,\Big/\left(\frac{n_1}{W_1}+\frac{n_2}{W_2}\right)$, and so on. Another difficulty in the way of this theory is that, as Pawlow has shown, positive rays can ionise a gas when their energy is as small if not smaller than that required by cathode particles for this purpose. In the case of a positive ray colliding with a corpuscle the masses of the particles are so different that only a small fraction of the energy of the moving particle can be transferred to the corpuscle; in fact, the equation shows that when M is large compared with m, ionisation will not occur unless $T=\frac{M}{4m}\cdot W_1$, while in the case of the collision between two corpuscles it might occur if $T=W_1$, thus if W_1 were 11 volts ionisation ought not to be produced by positive rays unless their energy were at least $1\,700 \times 11/4$, or 4 600 volts, whereas Pawlow has shown it occurs with positive rays when T is less than 11 volts. Another discrepancy is that if the corpuscles were knocked out by direct collision we should expect to find the maximum velocity of ejection dependent on the speed of the particle ejecting them, whereas the experiments seem to prove that there is no such effect.

The result seems to suggest that the ejection of a corpuscle by a cathode particle or a positive ray is not the result of these colliding directly with the corpuscle, but results rather from the effect of the collision with the atom regarded as a whole. This collision produces a kind of convulsion in the atom, the effect of which is to eject the corpuscle from a position in which it was in stable equilibrium under the forces inside the atom. When driven out of this position it comes under the action of repulsive forces which eject it from the atom and the velocity of projection will depend upon the forces inside the atom, and not upon the speed of the particle striking against it. We should expect this speed to be, on this view, the same whether the atom were struck by a positive particle or by a cathode ray. It is some confirmation of this view that the maximum number of ions produced by a cathode particle in its path through a gas is approximately equal to the number of collisions the particle would make with the atoms of the gas, if the atoms were of the dimensions usually assigned to them on the kinetic theory of gases. It would, however, seem likely that very rapid cathode particles which could penetrate right through the atom might be able to eject from it corpuscles with a greater velocity than that corresponding to 10 volts or so, which seems to be the limit for those ejected by more slowly moving cathode rays. The corpuscles ejected at a high speed must, however, be at most a very small fraction of the whole number ejected, for the photographs of the paths of the β particles taken by Mr. C. T. R. Wilson show that these paths are very rarely forked, as they would be if the atoms struck by the β particles gave out corpuscles moving at a speed comparable with that of the primary ones. Such particles would be able to travel a finite distance through the air, and would cause the ions produced by a β ray to be distributed somewhat as in Fig. 3. The actual photographs of the ions show, however, few traces of such branches, and indicate that the corpuscles projected from the atom have not sufficient speed to carry them through at an appreciable distance in gases at atmospheric pressure. This result raises some very interesting questions as to the production of Röntgen radiation by the impact of cathode rays. If we take the situation in air as revealed by the Wilson photographs to be typical of that occurring when cathode particles move through a collection of molecules of any kind, the cathode particle when it strikes against an obstacle dislodges from the atoms through which it passes slow secondary cathode rays, losing energy by this process in a more or less gradual manner, the amount of energy lost at each collision being but a small fraction of the energy of the cathode particle. It is hardly likely that encounters of this kind can give rise to Röntgen rays able to liberate corpuscles possessing a velocity comparable with that of the primary cathode particle. It seems to me more probable that the hard Röntgen rays produced by the impact of the cathode particles against the anti-cathode result from a process the inverse of that by which we supposed Röntgen rays to generate high-speed cathode rays. Let us suppose that at the stage in this process when the cathode

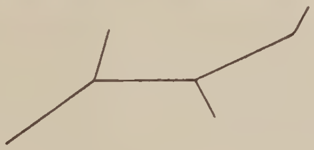


FIG. 3.

particle had acquired its final velocity its velocity were reversed, so that it retraced its path, and the whole process was reversed. The result would be that we should end by getting to the state which existed before the Röntgen ray struck the atom—*i.e.*, we should get the closed tube of electric force which on this view constitutes a Röntgen and the cathode particle that was originally free would be joined up in an atom with an equivalent charge of positive electricity. The cathode particle would cease to be a cathode particle and would be imprisoned in an atom, and thus the generation of a pulse of hard Röntgen radiation would be the swan's song of the cathode particle, the birth of a Röntgen ray involving the death of a cathode particle. The hardness of the Röntgen rays would depend upon the energy of the cathode particle; thus, those particles which got imprisoned before they had liberated many ions would produce harder Röntgen rays than those which only did so after losing a large part of their energy by ionising the atoms through which they pass. Mr. Wilson's photographs show that most of the cathode particles go on until they produce considerably more ions per unit length at the end of their path than they did at the beginning, showing that at the end their energy is considerably smaller than it was at the beginning. Thus, a large number of cathode particles remain free until they have lost a considerable part of their energy, as these give rise to softer Röntgen rays than those which have not lost energy, we should expect that the Röntgen rays would be very far from homogeneous, and would contain a considerable proportion of comparatively soft rays.

There should also be another kind of radiation produced by the impact of cathode rays. We have seen that these expel from the atoms corpuscles with a velocity not exceeding that due to 10 or 11 volts. Now the sudden starting of these 10 volt corpuscles ought to produce radiation, which, if Planck's view as to the relation between frequency and energy were to apply to this case, would be in the Schumann region. As the speed of these particles does not depend much on the speed of the primary cathode rays or the nature of the substance, we should expect to get a radiation of much the same type whatever the speed of the cathode rays or the material they struck against. I am not aware that any invariable radiation of this kind has ever been observed. It would not be likely to be able to ionise such gases as hydrogen or oxygen, which have ionising potentials of more than 10 volts. It might, however, be able to ionise mercury vapour, for which only 5 volts are required.

In many respects the ionisation of gases by the impact of cathode particles shows the same characteristics as the emission of secondary cathodic radiation when a metal plate is bombarded by cathode rays. This effect has been studied by Gehrts ("Ann. der Phys.," 36, p. 995) and Campbell ("Phil. Mag.," Aug., 1914). There is no secondary cathodic radiation until the velocity of the primary rays exceeds 11 volts. It then increases rapidly with the speed of the positive rays, and attains a maximum when the speed corresponds to about 300 volts; it then diminishes as the voltage increases. The velocity of the secondary rays is less than that due to 11 volts, and does not depend on the velocity of the primary rays, nor the nature of the material against which they strike. In all these respects the effects are analogous to those obtained when a gas is ionised by cathode rays, and indeed it seems clear that the physical processes going on in the two cases are identical—viz., the ionisation of the atoms. In one case the atoms ionised are those of a gas, and in the other those of a metal or, perhaps, gas absorbed in the metal. The fact that the secondary radiation does not begin until the energy in the primary rays have the ionising potential for hydrogen suggests, as Campbell has pointed out, that the secondary radiation may come from a film of hydrogen condensed on the surface of the metal, and that the curves obtained may really be those for the ionisation of hydrogen and not for the atoms of the metal. Particles at a higher speed might be expected to penetrate the layer and reach the metal. It would be interesting to see whether there is the same connection between ionisation of gases and secondary cathodic radiation at high speeds as there is at low. The rate at which both the secondary cathodic radiation and the ionisation of a gas increases with the energy of the incident cathode rays is very rapid when this energy corresponds to about 11 volts, the maximum energy required to ionise the gas. This ionisation may be regarded as the expulsion from the atom of the corpuscles which are most easily ejected; there are probably in the atom other corpuscles, more deeply seated which demand larger amounts of energy for their expulsion. In this case we should expect to find another stage, at which the ionisation would increase rapidly with the energy of the incident cathode rays. No experiments, as far as I am aware, have been published which give indications of such a stage until the energy of the cathode rays is sufficient to excite the characteristic radiation of the metal against which they strike. The experiments do not, however, extend over a very wide range of velocities of the primary rays. In Gehrts' experiments, for example, the maximum energy of the primary cathode rays was only that corresponding to about 600 volts. I am at present engaged with experiments on a point somewhat similar to this. Cathode rays, even when their energy does not exceed 50 or 60 volts, produce, when they strike against a target, appreciable amounts of very soft Röntgen radiation, and the experiments I am making are measurements of the amounts of this radiation when metals are bombarded with cathode rays of different speeds. If the atom contains a series of rings of electrons, then for each ring we should expect to get a special type of characteristic Röntgen radiation. This ought to make itself apparent by an abnormal increase in the radiation produced by the incident cathode rays when their energy passes through the values required to detach a corpuscle from any one of the rings: thus, if we can detect these increases we ought to be able to measure the number of rings in the atoms of the different chemical elements. The experiments are not yet concluded, but I hope on a future occasion to bring the results before the Society. I may mention, in passing, that the impact of positive rays, as well as of cathode rays, against a plate of metal gives rise to a very soft type of Röntgen radiation.

A very important point about the velocity of the slow corpuscles emitted when substances are bombarded by cathode rays is that apparently it does not depend on the nature of the substance bombarded. It is to be noticed, however, that these substances have nearly always been in the solid state and liable to be coated with films of gas: the corpuscles may come from these films and not from the metal, so that the evidence on this point is not conclusive. More to the purpose would be measurements of the velocities of the corpuscles from different gases, especially from those which, like helium and nitrogen, require very different amounts of energy to ionise them.

Some ionisation seems to be produced by positive particles when their energy is less than that required by cathode rays for ionisation. When once the cathode rays, however, do begin to ionise they produce far more ions than positive particles of equal energy. Another case when we have ionisation produced by the impact of bodies of molecular dimensions is that of hot gases. In a gas at the temperature of 2,000° C., the average kinetic energy of the molecules is that due to the fall of the ohmic charge through about 0·25 volt; hence, the number of molecules which possessed energy corresponding to 11 volts would be a fraction of the order ε^{-44} of the whole number of molecules: a gas in which the ions were in this proportion to the molecules would have quite measurable conductivity. If, however, the hot gas were helium, which, according to Franck and Pohl, requires about 22 volts to ionise it, the particles possessing this amount of energy would only be ε^{-88} of the whole number, and this fraction of ions would not possess appreciable conductivity. It would be interesting to see if the conductivity of hot helium was very much less than that of hot hydrogen. The greater part of the ionisation of hot gases occurs at the junction of the gas with hot solids, and it seems reasonable to suppose that gas condensed in a layer on the surface of a conductor would be more easily ionised than the gas in a free state. It would seem, however, from recent experiments by Campbell that a platinum plate, probably coated with a layer of hydrogen is not more easily ionised by cathode rays than free hydrogen.

We know that one part of the process of ionisation consists in the detachment of a corpuscle, but what happens to the rest of the molecule from which the corpuscle is detached? In the case of fast cathode rays we must remember that we have far more energy available than that which is usually supposed to be required for the dissociation of the molecule into atoms. When we study by the positive ray method the ions produced in a gas through which the electric discharge is passing we always find charged atoms of the gas through which the discharge is passing often, though not invariably, accompanied by charged molecules of the same gas. In this case, however, we have moving positive particles as well as cathode rays, and it might be thought that the charged atoms were produced by the positive rays, the charged molecules by the cathode rays. To test this point I used a discharge tube whose cathode consisted of a spiral of tungsten wires, the positive rays passing through the spiral. By heating the tungsten wire to a white heat it could be made to give out a large output of negative corpuscles, and so when the spiral was hot a larger proportion of the current would be carried by the negative particles than when it was cold. If, then, the cathode rays only produced charged molecules and not atoms the ratio of the charged molecules to the charged atoms would be greater when it was hot than when it was cold. I found, however, that the proportion of charged molecules of hydrogen to charged atoms was less for the hot tungsten than the cold, and hence I conclude that ionisation by fast cathode rays is frequently accompanied by the dissociation of the molecule into atoms. Whether this is so or not, when Röntgen rays expel high-speed corpuscles from gases through which they pass is a question on which, as far as I know, we have at present no evidence.

ABSTRACT.

Ionisation is the process by which ions—particles charged with electricity—are produced in a solid, liquid or gas. This address is confined to the consideration of ions in gases and deals with two questions—(1) the nature of the ions, (2) the process by which they are

produced. The evidence as to the nature of ions is derived from experiments on their mobility which have shown :—

a. The mobility of a positive ion depends only on the gas through which the ions are moving and not on the nature of the gas out of which the ions are formed.

β. The mobility of the ions in a gas at constant density is independent of the temperature.

γ. There are a considerable number of gases in which the mobility is very approximately inversely proportional to the square root of the density of the gas.

δ. In the case of negative ions there is an abnormal increase of mobility when the pressure is reduced below a certain value, and there is some evidence that this is also the case for positive ions at very low pressures.

Two theories of the mobilities of ions were considered, one founded on the view that the action between ions and molecules is analogous to impacts between hard elastic spheres, the other on Maxwell's theory of forces between ions and molecules varying inversely as the fifth power of the distance between them.

It is shown that *a* follows from the second theory provided the ion is a cluster whose mass is considerably greater than that of a molecule of the gas through which it is moving. On this supposition it follows also from the first theory if we suppose in addition that all ions in a given gas are of the same size.

(*β*) follows at once from the second theory : to explain it on the first theory we must suppose that the size of the ion varies with the temperature in a definite way. The necessary relation can be deduced from thermodynamical principles if we suppose that the force between an ion and a molecule is analogous to that between a charged point and a sphere which is either a conductor of electricity or has a high specific inductive capacity.

(*γ*) requires on theory one that the ions in these gases should be of the same size, on theory two that the molecules of these gases should exert the same force on a charged point at a given distance.

(*δ*) follows on either theory if the ion dissociates at low pressures so that free corpuscles are present in the gas.

With regard to the process of ionisation, the first stage of this in the vast majority of cases consists in the detachment of an electron or corpuscle. Evidence as to the method by which this takes place is afforded by determinations of the velocity with which the electrons are ejected from the body.

In the case of ionisation by light or Röntgen rays, this velocity depends primarily on the wave-length of the radiation, not upon its intensity, nor, at any rate to any great extent, on the nature of the molecule from which the corpuscle is ejected. This velocity is far greater, even when every allowance is made for resonance, than can be accounted for if we suppose that the energy of the light is uniformly distributed, and that the corpuscle acquires its velocity by the action on it of the electric force in the wave. Another explanation not open to these objections was put forward.

When ionisation is due to the action of moving electrified particles, whether positive or negative, the results are quite different. The velocity of the ejected particles (δ-rays, as they are sometimes called) does not seem to vary much, if at all, with the velocity of the particles which eject them, and is of the same order whether these particles are positive rays or the much swifter cathode rays. The method of ejection by the impact of such particles was considered, and suggestions as to a possible theory and some of its consequences thrown out.

Dr. R. T. **Glazebrook**, in moving a vote of thanks to the President, said that one expected, when listening to Sir J. J. Thomson, to be carried to the bounds of knowledge by one who had taken no small part in the extension of these bounds, and he was confident that none of those present had been disappointed in that expectation. He asked the President, on behalf of the Society, to allow his address to be published in full in the " Proceedings."

Dr. C. **Chree** seconded the vote of thanks, which was carried with enthusiasm.

PUBLICATIONS OF THE PHYSICAL SOCIETY

THE SCIENTIFIC PAPERS
OF THE LATE
SIR CHARLES WHEATSTONE, F.R.S.

Demy 8vo, cloth. Price 8s.; to Fellows, 4s.

Uniform with the above.

THE SCIENTIFIC PAPERS
OF
JAMES PRESCOTT JOULE, D.C.L., F.R.S.

Vol. I. 4 Plates and Portrait, price 12*s.*; to Fellows, 6*s.*
Vol. II. 3 Plates, price 8*s.*; to Fellows, 4*s.*

PHYSICAL MEMOIRS.

PART I.—VON HELMHOLTZ, On the Chemical Relations of Electrical Currents. Pp. 110. *Price 4s.; to Fellows, 2s.*

PART II.—HITTORF, On the Conduction of Electricity in Gases; PULUJ, On Radiant Electrode Matter. Pp. 222. *Price 8s.; to Fellows 4s.*

PART III.—VAN DER WAALS, On the Continuity of the Liquid and Gaseous States of Matter. Pp. 164. *Price 8s.; to Fellows, 4s.*

REPORT ON RADIATION AND THE QUANTUM-THEORY
By J. H. JEANS, M.A., F.R.S.

Price 6s.; to Fellows, 3s. Bound in Cloth, 8s. 6d.; to Fellows, 5s. 6d.

PROCEEDINGS.

The "Proceedings" of the Physical Society can be obtained at the following prices:—

Vol. I. (3 parts) bound cloth, 15*s*
Vols. II., IV. V., XXIII. & XXV. (5 parts each), bound cloth, 23*s.*
Vols. III., VI. to XII. & XXII. (4 parts each), bound cloth, 19*s.*
Vol. XIII. (13 parts, each containing Abstracts), bound cloth (without Abstracts), 47*s.*
Vols. XIV. & XV. (12 parts, each containing Abstracts), bound cloth (without Abstracts), 23*s.*
Vols. XVI. & XIX. (8 parts each), bound cloth, 35*s.*
Vols. XVII., XVIII. & XXI. (7 parts each), bound cloth, 31*s.*
Vol. XX. & XXIV. (6 parts), bound cloth, 27*s.*

Most of the parts can be purchased separately, price 4*s.* by post 4*s.* 3*d.* Fellows can obtain the *Proceedings* (in parts) for their personal use at half the above prices.

ABSTRACTS OF PHYSICAL PAPERS
FROM FOREIGN SOURCES.

VOLS. I. (1895), II. (1896), and III. (1897), 15*s.* each; to Fellows, 7*s.* 6*d.* each.

Strong cloth cases for binding the "Proceedings," price 1s. 6d. each, post free.

BLAKESLEY, T. H. A Table of Hyperbolic Sines and Cosines. *Price 1s. 6d.; to Fellows, 9d.*

LEHFELDT, R. A A List of Chief Memoirs on the Physics of Matter. *Price 2s.; to Fellows, 1s.*

Applications for the above Publications should be sent direct to
"THE ELECTRICIAN" PRINTING & PUBLISHING CO., LTD.,
1, 2 AND 3, SALISBURY COURT, FLEET STREET, LONDON.

CONTENTS.

PAGE

I. The Production of Soft Röntgen Radiation by the Impact of Positive and Slow Cathode Rays. By Sir J. J. THOMSON, O.M., F.R.S. 1

II. On the Measurement of the Temperature Coefficient of Young's Modulus for Metallic Wires, with Special Application to Nickel. By E. PHILIP HARRISON, Ph.D., F.R.S.E., Indian Educational Service, Professor of Physics, Presidency College, Calcutta 8

III. A Bridge for the Measurement of Self-Induction in Terms of Capacity and Resistance. By DAVID OWEN, B.A. (Cantab.), B.Sc. (Lond.), Lecturer in Physics, Birkbeck College, London 39

IV. On the Coefficient of Diffusion in Dilute Solutions. By BASIL W. CLACK, B.Sc., Lecturer in Physics at Birkbeck College 56

V. Note on the Conduction of Electricity at Point Contacts. By A. F. HALLIMOND, Geological Survey and Museum, Jermyn Street 70

VI. Thermal Conductivity. Part II.: Thermal Conductivity of Badly-conducting Solids. By THOMAS BARRATT, A.R.C.S., B.Sc. 81

VII. Ionisation. By Sir J. J. THOMSON, O.M., F.R.S. 94